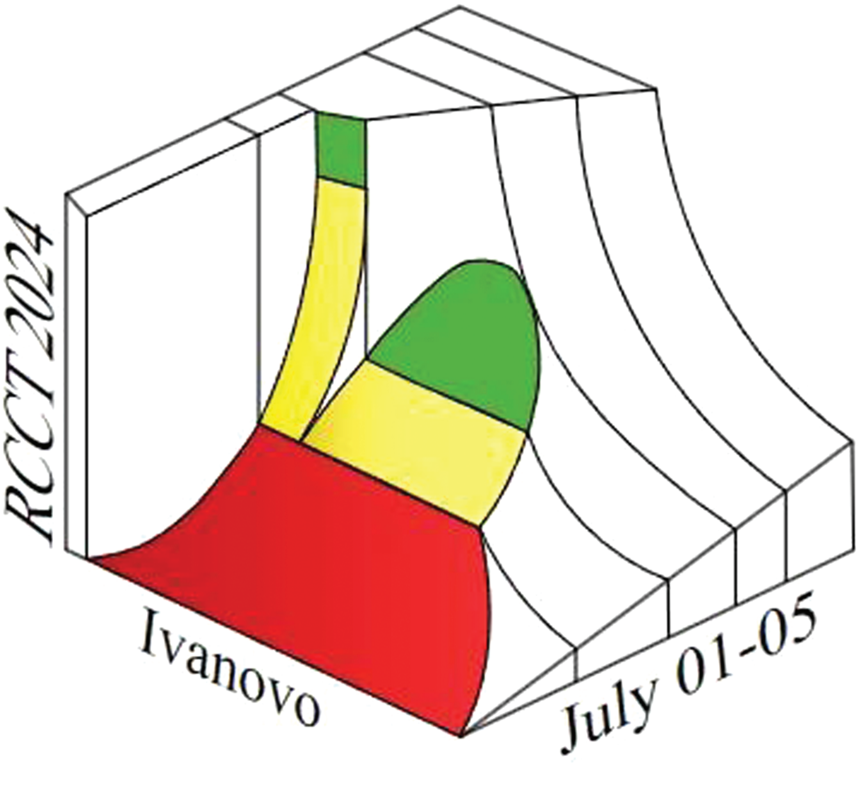
XXIV International Conference on Chemical Thermodynamics in Russia

July 1-5, 2024
Ivanovo, Russia



RCCT-2024

BOOK OF ABSTRACTS

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PREFACE

This book contains the abstracts of presentations at the XXIV International Conference on Chemical Thermodynamics in Russia (RCCT-2024).

The XXIV International Conference on Chemical Thermodynamics in Russia (RCCT-2024). Conferences on chemical thermodynamics are among the largest scientific events in Russia. The first conference of the series – “The All-Union Conference on Calorimetry" – opened in 1961 and was then held every two-three years until 1977. In 1979 it was renamed "The All-Union Conference on Calorimetry and Chemical Thermodynamics" and was held regularly until 1991. Then there was a long pause in the conference history until 2002, when the conference tradition was revived with the first “International Conference on Chemical Thermodynamics in Russia” in Saint Petersburg. Since then the RCCT International Conferences have been organized every two years in large scientific centers of Russia, including Moscow (2005, 2013), Saint Petersburg (2002, 2019), Ivanovo (2007), Kazan (2009, 2022), Samara (2011), Nizhny Novgorod (2015), and Novosibirsk (2017).

Every RCCT is a unique and important scientific event both for the Russian and international thermodynamic communities. The conference traditionally covers all aspects of chemical thermodynamics from fundamental to applied problems, including multidisciplinary approaches and related fields of science. RCCT2024 is to take place in the year of the 300th anniversary of the Russian Academy of Sciences.

The conference brings together around 300 scientists from 9 different countries; many of them are young researches, including undergraduate and graduate students. Three junior poster awards for the best poster presentations and three junior oral presentation awards have been established by the organizers. The scientific program of RCCT2024 includes plenary and keynotes, 3 parallel sessions of oral presentations and 2 poster sessions. These contributions reflect the latest trends in Chemical Thermodynamics, including the development and application of theory, new experimental techniques and computer simulation for a variety of different systems.

On behalf of the organizers,

Michael G. Kiselev, RCCT-2024 Vice-chair

PLENARY
LECTURES

ATTRIBUTES OF SUPERCRITICAL FLUID

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The exploration of the supercritical state has a rich historical background. Initially, it was believed that a supercritical fluid is a mixture of "liquidons" and “gasons” representing a combination of "liquid" and "gas" phases, which were thought to be distinct entities [1]. Starting with Van der Waals, it gradually became clear that the supercritical fluid consists of the same molecules as both gas and liquid. It was considered to be completely homogeneous and lacking any interesting features. However, recent studies have shown that when crossing the Widom line, the properties of the fluid rapidly change, such that on one side, the fluid exhibits liquid-like properties, while on the other, gas-like properties [2]. The structure of the supercritical fluid is a mixture of micro-objects of liquid-like and gas-like types [3]. The Widom line is usually determined by the maximum of response functions. The problem is that there are many different response functions. Only up to a temperature of 1.1 T_c their maxima coincide, but beyond that, they quickly diverge in different directions [4]. The phase behavior of the fluid near the critical point is described based on the renormalization group approach. This approach explains the behavior near the critical point but does not consider the molecular structure. In the supercritical region, something reminiscent of a liquid-gas phase transition is observed, and there are indications of microscopic objects similar to liquid and gas. It turns out that the states near the critical point and in the supercritical region are fundamentally different, although thermodynamically close. It is necessary to understand how these two states transform into each other, identifying the stages of structural transformation.

The Two-Phase Hierarchical Model [5] addresses these questions, describing the phase behavior of the fluid both near the critical point and in the supercritical region. At the first stage, upon decreasing temperature and pressure, the supercritical fluid separates into "microdroplets" and "microbubbles" (supercritical mesophase). Consequently, we can conclude that the separation into liquid and gas initiates at the microscopic level. These microscopic-scale objects form branched clusters that intertwine with each other, creating a unique type of structure. After this, objects of the previous level give rise to objects of the next levels, forming a multi-level hierarchical structure. As the critical point is approached, the number of levels tends to infinity. The boundaries of the supercritical mesophase are estimated to be approximately 10% above the critical temperature, corresponding to about 1.6 times the critical pressure. Near the critical temperature, the densities at the boundaries of the supercritical mesophase are approximately 75% and 125% of the critical density.

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The research was supported by the State programs №AAAA-A19–119013190038-2, №122022800272–4.

A NEW APPROACH TO CALCULATING MECHANICAL STRESSES IN MOLECULAR SYSTEMS FROM THE FIRST PRINCIPLES OF STATISTICAL PHYSICS. FROM GENERAL THEORY TO SPECIFIC PROBLEMS

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To describe the forces acting between macroscopic surfaces in a fluid, we need to have a stress tensor that is consistent with the thermodynamic properties of the fluid. In this talk, we will discuss recent approaches recently developed by us [1-4] for calculating the stress tensor in inhomogeneous fluids using the thermodynamic potential as a functional of certain scalar order parameters such as concentrations and electrostatic potentials. Special attention will be given to applications in heterogeneous ionic fluids, such as room temperature ionic liquids, electrolyte solutions, and polyelectrolytes. We will also discuss the application of this approach to calculating surface tension at the interface between an aqueous electrolyte and air or dodecane, as well as beyond the Onsager-Samaras limit.

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THERMODYNAMICS OF DRUG POLYMORPHISM

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The problem of polymorphism of organic compounds, including medical drugs, is linked to the influence of drug crystalline packing on its bioavailability and, respectively, on biological activity. Besides, polymorphism is linked to the problem of molecular recognition, which draw relationship of different crystal patterns of the same compound with the conditions of their preparation including the solvent or guest involved in crystallization. One of the stages of testing an organic compound as a medical drug is the search for all its possible polymorphs. This testing is complicated by the lack of methods for the reproducible preparation of metastable forms, which for this reason are called “disappearing”.

This work proposes a solution to the problem of reproducible preparation of metastable polymorphs for substances capable of forming inclusion compounds (solvates). The method is based on the use of solid-state exchange/repulsion of guest in inclusion compounds [1-3]. As a result, mostly thermodynamic control is reached for the process producing metastable polymorphs, which enables milder conditions for their preparation without transition to a more stable form [3]. In a number of cases, absolute selectivity of molecular recognition was observed with the formation of a metastable polymorph after the inclusion and release of only one guest compound by the solid host. This is a kind of smart property, in which the host crystal packing selectively remembers the previously included guest. The applicability of the developed method has been shown for a number of calixarenes [1-3] and drugs such as indomethacin [4] and phenylbutazone. The prepared polymorphs were characterized by fast scanning chip calorimetry, which is used to determine the melting point and fusion enthalpy of thermally unstable substances, as well as metastable polymorphs for microcrystals weighing several dozen nanograms [2-4].

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The financial support of the Strategic Academic Leadership Program of the Kazan Federal University “Priority-2030” is gratefully acknowledged.

UNRAVELING LOCAL STRUCTURE DYNAMICS IN IONIC LIQUID-SOLVENT MIXTURES: INSIGHTS FROM SPECTROSCOPY, SIMULATION, AND QUANTUM CALCULATIONS

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Ionic liquids (ILs) are a diverse group of substances that attract considerable scientific interest due to their many beneficial properties. They are commonly used alongside molecular solvents with varying characteristics across numerous applications. However, understanding the intricate local structure within such mixed systems, influenced by factors like composition and constituent properties, remains a key focus of ongoing research. In this contribution, we will summarize findings from vibration spectroscopy, NMR chemical shift analyses, and time resolved Kerr effect studies on specific IL-solvent combinations. Subsequently, we will present insights from molecular dynamic simulations aimed at interpreting these experimental results. These simulations utilize tailored statistical distribution functions to capture nuanced information about local structure, which conventional averaging methods may overlook. Noteworthy among these statistical distributions are radial and orientational distribution of nearest neighbors, Voronoi polyhedral analysis, and density-based methodologies. Additionally, we will share recent data on interpreting NMR chemical shifts through quantum calculations. A new comprehensive method is proposed to reveal the evolution of bonding characteristics between the interacting components of the mixture. Particular attention is paid to the cation- anion and cation-solvent interactions, validated against theoretical and how the description of their electronic density can helps to interpret the experimental ^{1}H NMR chemical shifts. For the target ILs-acetonitrile mixtures the bonding interactions nature of bonding interactions is analyzed in terms of QTAIM, NBO and Non-covalent Interactions (NCI) analysis techniques.

SURFACE AFFINITY OF SIMPLE IONS IN AQUEOUS SOLUTIONS

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Salts of simple ions, such as alkali halides, are long known to be effectively repelled from the surface of water, as they increase rather than decrease the surface tension of their aqueous solution. In spite of this long-standing notion, it was shown at the turn of the Millennium both experimentally and by computer simulations that large, polarizable simple anions, such as I^-, are accumulated at the surface of their aqueous solutions. Refinement of the Onsager-Samaras theory confirmed that the surface affinity of simple, spherical ions increases with their size and polarizability. However, the seeming contradiction between the surface accumulation of such ions and the increase of the surface tension by their salts needs to be resolved.

We have performed a set of molecular dynamics simulations of the aqueous solutions of alkali chloride and sodium halide salts using both nonpolarizable and polarizable potential models, and analyzed the properties of the liquid surface using an intrinsic method, namely Identification of the Truly Interfacial Molecules (ITIM) [1]. This way, we could (i) see the variation of the different structural [2], and dynamical [3], and dipolar [4] characteristics of the particles pertaining to the subsequent molecular layers beneath the liquid surface; and (ii) calculate profiles of various quantities along the surface normal relative to the real, intrinsic, capillary wave-corrugated liquid surface rather than to the average, planar Gibbs dividing surface. The intrinsic treatment provided us with unprecedented details of the liquid surface, and revealed, among others, that the surface layer, consisting of I^- ions in an excess concentration, is followed by layers of its depletion, giving rise to a net negative surface excess, in accordance with the increase of the surface tension. The negative surface charge imposed by the surface accumulation of the I^- ions is compensated by a diffuse layer of the cations, giving rise to an electric double layer structure that is compatible with the Gouy-Chapman theory.

Our results indicate that the negative surface excess and surface tension increase of the iodide salts is caused by the fact that the effective repulsion of the small alkali cations from the surface overcompensates the surface accumulation of the large I^- ions. This finding gives rise to the question whether the combination of I^- with a sufficiently large simple cation results in a surface active simple salt. We addressed this issue in two ways. First, we showed by computer simulation that the fictitious salt in which the cation is identical, apart from the sign of its charge, from the I^- anion, is indeed surface active. This approach also enabled us to address the role of the charge sign in the surface affinity [5]. Second, we demonstrated by a combined experimental and computer simulation study that tetramethylammonium iodide, consisting of a quasi-spherical quasi-simple cation, is indeed mildly surface active [6].

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MOLECULAR COMPLEXES WITH PHOTOINDUCED ENERGY TRANSFER BASED ON DIPYRROMETHENE SERIES COMPOUNDS

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Currently, intensive research is underway in the field of creating and characterizing luminophores based on dipyrromethene coordination compounds. Special focus is directed towards exploring the utility of fluorescent sensors and hybrid materials derived from them across various scientific and technological domains, including environmental and medical-analytical monitoring. Addressing contemporary challenges in fluorescence sensing necessitates the development of novel, highly sensitive, selective, and cost-effective methods for rapid detection of micro- and ultra-microquantities of toxic and biologically significant analytes. These analytes encompass N- and O-containing as well as aromatic compounds in diverse *in vitro* and *in vivo* medium. Coordination compounds of *p*- and *d*-elements with dipyrromethene ligands are deemed as promising platforms for creating multifunctional fluorescent sensors. Significant attention will be devoted to a novel class of luminophores based on zinc(II) coordination compounds featuring tetradentate *bis*(dipyrromethene) ligands (H_2L) (Figure 1).

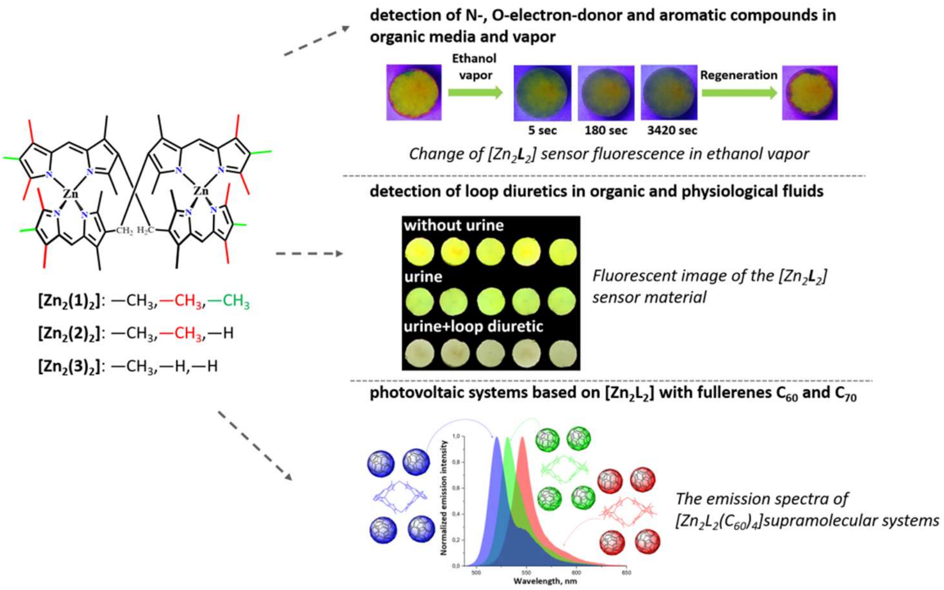

Figure 1. Fields of practical application of $[Zn_2\mathbf{L}_2]$.

The report will present the results of a study on molecular systems based on coordination compounds of *p*- and *d*-elements with dipyrromethene ligands, focusing on their applications in fluorescence sensing (Figure 1). To date, significant progress has been made in understanding the spectral response mechanisms of zinc(II) bis(dipyrromethenate)s with a wide range of molecular ligands. Promising areas of their utilization include: 1. fluorescent detection of N-, O-electron-donating, and aromatic compounds in organic media and gas phases; 2. fluorescent detection of loop diuretics in organic and physiological fluids; 3. development of photovoltaic systems based on zinc(II) bis(dipyrromethenate)s with fullerenes. Additionally, attention will be given to the application of machine learning methods in designing sensor compounds.

THERMODYNAMIC PROPERTIES OF C_{60} AND C_{70} FULLERIDES AND REDOX-ISOMERIC COMPLEXES OF THE TRANSITION METALS

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The donor-acceptor complexes of C_{60} and C_{70} fullerenes are actively used as materials with unusual optical, magnetic and electrical conductivity properties. The complexes with aromatic hydrocarbons as donor partners were synthesized and their physico-chemical properties were studied. As a result, the low-temperature dimerization of anion-radicals of the fullerene was detected on studying their thermal behavior. The data on the heat capacity and thermodynamic properties of crystalline fullerides are necessary as fundamental characteristics for new functional derivatives of C_{60} and C_{70} to understand the nature of the low-temperature dimerization of fullerene fragments as well as to detect the influence of organoelement groups on the stability of bonds between fullerene fragments in the low-temperature dimeric phase.

The basis for the creation of the molecular devices are systems with bistability (the ability of molecules to exist in two different electronic states under the influence of external influences: temperature, light, pressure, magnetic field). The most promising examples of transitions in bistable systems are spin-crossover (an externally induced change in the spin multiplicity of a metal) and redox-isomerism (the phenomenon of intramolecular ligand–metal electron transfer in metal complexes for which there are two stable valence states), first discovered in the early 1990s in crystals of cobalt *o*-semiquinone complexes. It was shown that external action causes a shift in the equilibrium of the mutual conversion of isomers that differ in structure, valence and spin states of the metal and ligands. The revealed redox-isomeric transformation is accompanied by a phase transition. The unique physico-chemical properties of the complexes associated with the existence of various valence tautomeric forms currently determine progress in the field of creating promising materials for microelectronics.

Thermodynamic properties of C_{60} and C_{70} fullerides and redox-isomeric complexes of the transition metals were determined by a precise low-temperature adiabatic calorimetry in the range of 6–350 K. In particular, the temperature dependences of the heat capacities of compounds were experimentally determined for their various physical states. The reversible intramolecular transfer of the metal–ligand electron was revealed; its thermodynamic characteristics were determined; the values of the quantities depending on the structure and composition of the complexes were analyzed. A special attention is paid to the study of the nature of phase transitions accompanying intramolecular electron transfer by EPR spectroscopy and magnetochemistry methods. A set of the standard thermodynamic functions of the studied compounds was determined for the range from 0 to 350 K. The low-temperature heat capacity ($T < 50$ K) was analyzed using a multifractal model; some conclusions were made concerning the topology of the complexes structure. The practically important dependencies «thermodynamic property – composition» were established taking into account EPR spectra, magnetic properties and X-ray diffraction analysis data.

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (FSWR-2023-0025) and the scholarship of the President of the Russian Federation for young scientists and postgraduate students (SP-1369.2022.4).

THE INTERACTION BETWEEN MODEL BIOMEMBRANES AND THERAPEUTIC PEPTIDES THROUGH THE LENS OF PHYSICAL CHEMISTRY

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Therapeutic peptides are a novel and promising approach for the development of antimicrobial and anticancer agents[1,2]. Most of these antimicrobials (AMPs) and anticancer (ACPs) peptides act by inducing the cell membrane rupture and/or permeabilization. Understanding the molecular basis and the thermodynamics underling the interaction process with the membrane is mandatory for the development of new peptides with an improved antimicrobial/anticancer activity and low cytotoxicity. However, despite a large research effort, the dependence of peptides activity on the detailed molecular properties of both peptides and lipids is not fully understood. In this talk, I will present several examples showing how the physico-chemical approach can shed light on the peptide-membrane interaction revealing the peptide effect on the membrane microstructure and thermotropic properties.

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ON APPLICABILITY OF THE THERMODYNAMIC PHASE AND PHASE TRANSITION CONCEPTS TO NANOPARTICLES AND NANOSYSTEMS

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In relation to nanothermodynamics, one may face with negativity and two extreme points of view: 1) complete denial with reference to the initial concepts of the thermodynamic system and thermodynamic phase; 2) uncritical and inadequate extension of thermodynamic relations to nanoclusters of radius comparable to the atomic size. We have showed [1] that, with certain adjustments and limitations, the concepts of thermodynamic phase and phase transition are applicable to ensembles of metal nanoparticles, although for Lennard-Jones nanoparticles and other types of nanosystems, for example, for systems of micelles, the phase approach (the term was introduced by A.I. Rusanov [2]) may be less adequate or entirely inapplicable. At the same time, as we have shown earlier [3], the role of fluctuations at the nanoscale is significantly exaggerated. Phase transitions in nanoparticles are characterized by a number of specific mechanisms and patterns, including the much more noticeable role of continuous (surface) melting [4]. According to results of our molecular dynamics experiments, among the three commonly considered models of the nanoparticle melting (homogeneous melting, liquid shell, nucleation of liquid and growth), the latter is most adequate. However, our more adequate, as we believe, model corresponds to a combination of the continuous melting at the initial stage of the process with later almost instant disappearance of the crystalline core after its definite critical radius is reached.

The order-disorder transitions in binary and multicomponent nanosystems relate to segregation of their components. Thermodynamic methods are successfully used to predict surface segregation in binary metal nanoparticles [5]. On the one hand, the surface segregation complicates mechanisms of phase transitions in binary and multicomponent nanoparticles. On the other hand the surface segregation may be considered as a factor of self-organization, including the core-shell structure formation. The concept of a phase diagram has also been extending to nanosized objects [6], although such an extension is associated with a number of serious difficulties and unsolved problems.

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COMPENSATION RELATIONSHIP IN SOLVATION THERMODYNAMICS OF ORGANIC NON-ELECTROLYTES

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The linear relationships between the enthalpies and entropies changes, often called compensation relationships, are observed in various physicochemical processes. In this work the equivalent relationsips between the standard Gibbs energies (ΔG°) and enthalpies (ΔH°) of vaporization and solvation of organic non-electrolytes in various solvents are discussed:

$$\Delta_{\mathrm{solv/vap}}G^{\circ} = \mathrm{a}\ \Delta_{\mathrm{solv/vap}}H^{\circ} + b$$

A new approach to the analysis of this relationship is proposed. It is intended to reveal the reasons for the "chaotic" distribution of the values on $\Delta_{\mathrm{solv/vap}}G^{\circ}$ *vs.* $\Delta_{\mathrm{solv/vap}}H^{\circ}$ plot.

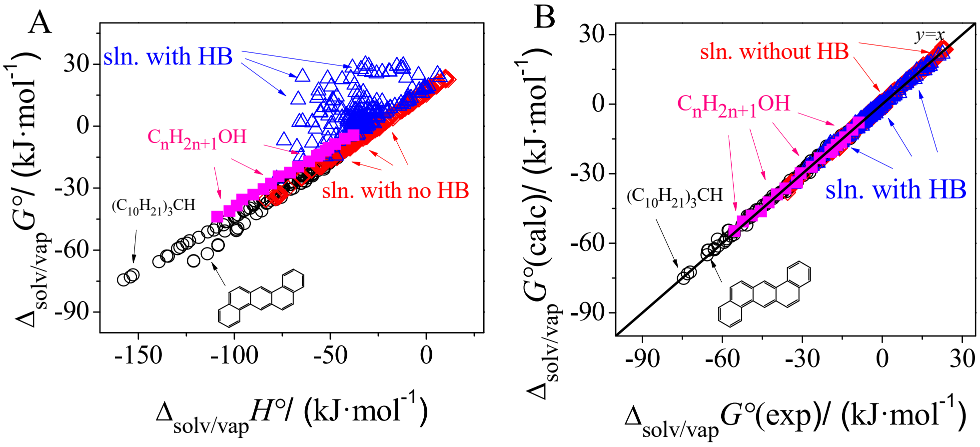

Figure 1. (A) The relationship between $\Delta_{\mathrm{solv/vap}}G^{\circ}$ and $\Delta_{\mathrm{solv/vap}}H^{\circ}$ of organic non-electrolytes (~2000 experimental datapoints). (B) The comparison of experimental ΔG° and the values calculated using the methodology proposed in this work.

The proposed approach is based on the idea of division of the thermodynamic functions of solvation of solute A in solvent S ($\Delta_{\mathrm{solv}}f^{\,\mathrm{A/S}}$) into 3 components: the thermodynamic functions of nonspecific, specific interactions, and solvophobic effect (Eq. 2):

$$\Delta_{\mathrm{solv}}f^{\,\mathrm{A/S}} = \Delta_{\mathrm{nonsp}}f^{\,\mathrm{A/S}} + \Delta_{\mathrm{sp}}f^{\,\mathrm{A/S}} + \Delta_{\mathrm{s.e.}}f^{\,\mathrm{A/S}} \qquad (2)$$

Earlier, we developed the ways for the quantitative determination of $\Delta_{\mathrm{sp}}f$ and $\Delta_{\mathrm{s.e.}}f$. In accordance with Eq. (1), A-S systems were divided into 4 types: (1) A and S are incapable of hydrogen bonding; (2) S is hydrogen-bonded but A is incapable of hydrogen bonding with S; (3) S is not hydrogen-bonded but A and S form hydrogen bond; (4) S is hydrogen-bonded and forms hydrogen bond with A [1].

For each type, the approaches that enable to understand the reasons for a scatter on the plot 1A and quantitatively estimate them are developed. The quality of such estimates was checked by comparison of calculated and experimental $\Delta_{\mathrm{solv/vap}}G^{\circ}$ values (Fig. 1B). Applications of the controlled relationships between $\Delta_{\mathrm{solv/vap}}G^{\circ}$ and $\Delta_{\mathrm{solv/vap}}H^{\circ}$ to calculating the thermodynamic functions of solvation, phase transitions, hydrogen bonding are presented.

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PREPARATION OF NANOPOROUS METALS BY MEANS OF HIGH-TEMPERATURE ELECTROCHEMICAL DEALLOYING

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Nanoporous metals are a new class of materials with promising application prospects in a wide variety of fields. Porous nano- and microstructures obtained by dealloying (chemical, vapor-phase, liquid-metal or electrochemical removal of a less noble metal) are a special subclass, which have a continuous framework of ligaments (ligaments), which can vary from a few nanometers to a few microns, as well as open porosity [1]. Such materials provide new opportunities for the design and development of new devices and products that have applications in catalysis, electrochemical energy, medicine, and environmental monitoring. Electrochemical dealloying has already been devoted to a large number of works performed in aqueous solutions, but there is almost much less information about molten salt and organic ionic media at elevated temperatures. This report will present a review of our works on electrochemical dealloying (anodic dissolution) of various alloys as Ag-Zn [2], Ag-Pd, Ag-Au-Pd [3], Pd-In [4, 5], Fe-Mn [6], Cu-Zn [7] in molten chloride eutectics of alkali metals, as well as in deep eutectic solvents (DES). Despite the diversity of properties of the initial alloys (intermetallides, solid solutions), it was possible to find the percolation mode of anodic dissolution both in molten salts and in DES, which led to the formation of nano- and microporous structures much faster than in aqueous electrolytes. The selectivity of the process is higher for potentiostatic electrolysis, however, galvanostatic regime has the advantage of speed. The results of XRD studies, scanning electron microscopy, electrochemical characteristics and data on some catalytic reactions will be presented. Nanoscale porous materials (of the order of 100 nm) are obtained for ferromanganese samples at temperatures below or near the onset recrystallization temperature of iron (near 450 °C). The evolution of porous iron structures in this case up to temperatures up to 750°C is described. Increasing the dealloying temperature naturally leads to the activation of sintering processes with coarse-graining of ligaments up to closed porous structures [6]. Anodic dissolution of the PdIn made it possible to obtain a coherent nanoporous structure consisting of congruent Pd_2In and Pd_3In compounds in 2:1 ratio [4]. The observation was made of an interesting feature of surface oxidation of the obtained nanoporous iron samples, namely, the formation of wüstite nano-whiskers after finishing dealloying already at room temperature [8].

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ALTERNATIVE APPROACHES TO THE ANALYSIS OF THERMODYNAMIC STABILITY CONDITIONS AND THEIR FORMULATIONS

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The conditions of thermodynamic stability, together with the conditions of equilibrium, form the basis, the foundation of phenomenological thermodynamics. In a certain respect, they occupy a central place, since they determine the relationship between equilibrium and non-equilibrium theories, and it is in the formulations of stability that the consequences of the second law are most clearly used and manifested. Nevertheless, the role of stability conditions in modern literature is underestimated. This is partly what Prigogine meant, pointing out that the application of thermodynamics is essentially limited to the analysis of equilibrium processes. Let me remind you that even in the titles of I. Prigogine's books there is the word "stability" [1]. The presented report will provide a brief overview of classical and some modern works. Further, the variants of the existing formulations of thermodynamic stability conditions are discussed, with their critical analysis.

Special attention is paid to determining the boundary of thermodynamic stability, respectively, the spinodal condition and the first critical phase equation. This part of the lecture will present our recent work and some earlier results. References on selected publications are listed below [2-4]. The variants of thermodynamic stability conditions obtained using the approach of contact geometry are considered, including in relation to the formulations of the Le Chatelier – Brown principle. These results are compared with more traditional representations in the form of chains of thermodynamic inequalities. For systems with chemical reactions, we present the approach we have developed to assess stability and its boundaries in the case of "non-chemical" equilibrium disturbances. Accordingly, the conditions of stability boundaries in the case of chemical interactions in a multicomponent system are considered. Finally, a more correct approach to the analysis of perturbation processes (virtual and real) will be presented, taking into account the non-equilibrium nature of these perturbations. On this basis, the forms of stability conditions and stability boundaries are obtained, which differ somewhat from the traditional ones.

In the last part of the lecture, some examples of applications of stability conditions to the analysis of experimental data will be presented, and prospects for the development of thermodynamic modeling methods are proposed.

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The author expresses gratitude to his co-authors of a number of recent works in the field of stability theory, Dmitry Gromov, Georgy Misikov and Maria Toikka, their participation and views on the problems made it possible to touch upon some new aspects and identify promising tasks of the theory. The lecture is dedicated to the 300th anniversary of Saint Petersburg State University's founding.

TO THE 100 ANNIVERSARY OF CHEMICAL THERMODYNAMICS LABORATORY AT MSU: PROGRESS IN EXPERIMENTAL AND COMPUTATIONAL METHODS

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At the end of 2023, the Laboratory of Chemical Thermodynamics, originally called the Laboratory of Galurgy, celebrated its centenary. Being one of the oldest chemical laboratories of Moscow State University, it was founded by Professor A.V. Rakovsky.

For a hundred years, the objects of research have been systems of various natures: salt systems, alloys, ceramics, organics, and water-organic mixtures. But they were united by a single principle - the possibility of practical application for the development of new and optimization of existing technologies to produce substances and materials.

In the early days of the laboratory's existence, one of the main directions was the development of methods for obtaining pure salts for scientific and analytical purposes. At the beginning of the 21st century, the laboratory returned to this topic, but at a higher level of research aimed at finding solutions to complex modern problems. In the 30-60s, the laboratory under the leadership of Ya.I. Gerasimov began to develop experimental studies of thermodynamic properties necessary for theoretical calculations of processes with non-ferrous, refractory, rare-earth metals, and semiconductor compounds. For a series of works on the thermodynamics of semiconductors Professor G.F. Voronin, who headed the laboratory from 1976 to 2015, was awarded the USSR State Prize in the field of science and technology (1981) as part of the authors team. In the 70-90s of the last century, laboratory staff actively developed electrochemical methods for determining the thermodynamic properties of various systems, among which the undoubted leader was superconducting phases in ceramic systems. At the same time, thermodynamic modeling of different dimension and nature systems was separated into a separate area, which in the following years became one of the most popular and actively developing areas of research.

The main direction of modern research activity is the combination of experimental and computational studies, which makes it possible to realize all the advantages of chemical thermodynamics for solving various fundamental and applied problems. Over the past twenty years, the laboratory has developed a number of new methods and created original equipment for determining thermodynamic properties. Dozens of different systems have been studied that are promising to produce new types of functional and structural materials, the development of new technologies for the separation and purification of substances, and the processing of industrial waste. Laboratory staff has developed several software products, which are widely used in scientific research and the educational process both in our country and abroad. The PhDi and TERNAPI software systems, Cpfit program implement new methods and approaches developed in the laboratory - the convex hull method for modeling heterogeneous systems and a combination of Planck-Einstein functions for approximating the temperature dependences of thermodynamic functions.

Successful experience in modeling systems of various natures and dimensions allowed the laboratory staff to solve the ambitious task of creating a domestic software package for calculating phase and chemical equilibrium. This project has united various thermodynamic teams of the Russian Federation within the framework of a single consortium of Universities and Institutes of the Russian Academy of Sciences, which gives reason to hope that all plans will be successfully implemented.

Investigation was supported by RSF (grant № 23-13-00138).

MODELING OF SOFT MESOSCOPIC STRUCTURES: OVER THE 30 YEARS OF MOLECULAR-THERMODYNAMIC LANDSCAPE

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Molecular Thermodynamics emerged in the nineteen fifties [1], as a distinct field aimed at providing practical tools for the description of phase equilibria and thermodynamic properties of macroscopic phases in engineering applications.

For the mesoscopic fluids, the birth of molecular thermodynamic approach may be attributed to the early nineties, with the advent of heuristic molecular-thermodynamic models of aggregation for the micellar solutions [2, 3]. Although lacking theoretical rigor, molecular thermodynamics of aggregation serve as a fruitful and unifying approach to seemingly unrelated issues, such as asphaltene drop-out from crude oils, charge regulation in polyelectrolyte membranes under deformation, effects of added salt on the viscosity of solution, ion exchange in Nafions, emulsification failure, formation of spatial networks, swelling of gels, and separation of biomolecules.

In this work, we illustrate and discuss application of molecular thermodynamic aggregation models, including the classical model and some of the more recent approaches, e.g., iSAFT, to a variety of mesoscopic fluids, also giving an account of the contribution from our team [4] to the field. Specifically, we demonstrate how to address all of the listed above seemingly different topics and show the results.

Discussing the modern trends in the development of Molecular Thermodynamics for mesoscopic fluids, we stress the growing impact of rigorous statistical-mechanical theories [5] on architecting the models [6, 7].

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PARTICULARITIES OF THE FORMATION MECHANISM OF AND THERMODYNAMIC PROPERTIES OF LAYERED MATERIALS CONSTRUCTED ACCORDING TO THE BLOCK PRINCIPLE

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Layered oxide materials to be of great interest from the point of view of a wide range of their functional properties (magnetic, electrical, catalytic), are intensively studied and have already found application in various fields of science and technology. Last years layered oxides attract attention as high efficient photocatalysts in reactions of hydrogen production and using as precursors for the preparations of nanosheets and nanocomposites [1,2]. The search for new materials faces difficulties in the synthesis of single-phases and their instability. All this determines the importance of the information on formation mechanism of layered structures built by block principle, the limits of their thermal and chemical stability. Moreover, thermodynamic properties of these materials continue to be rather scarce even such kind of information is an essential for the understanding of many phenomena and application.

The report will consider the influence of peculiarities of layered structure on heat capacity, thermodynamic properties, stability, photocatalytic activity, and ability for the exfoliation for several classes of perovskite-like layered oxides with different thickness of perovskite layers and different cationic content in perovskite blocks and interlayered space. It will be considered the mechanism of the formation of layered structures from blocks of different structures.

On the example of $Ln_2SrAl_2O_7$ (Ln = La – Ho) it will be demonstrated the dependence of the formation mechanism on the nature of Ln, the dependence of their stability on the positional distribution of cations over two nonequivalent positions in different blocks of layer structure with heterovalent isomorphism, which could effectively reduce the probability of fluctuations in crystal composition as precursors to the phase separation and instability. Special attention will be paid to the formation of fully cation-ordered oxides $A_2Ln_2Ti_3O_{10}$ (A= alkaline metal) and their organo-inorganic hybrids promising for the photocatalytic production of hydrogen from aqueous organic solutions, including biomass derivatives [1]. Mobility of cations in interlayer space explains participation of their protonated forms in reactions with amines and alcohols by the intercalation and grafting [2].

The overview on heat capacity (6 – 350 K) and standard thermodynamic properties of cation-ordered layered perovskite-like titanates $NaLnTiO_4$ and $A_2Ln_2Ti_3O_{10}$ (A=H, Na, K; Ln=La, Nd, Gd) will be present. The nature of alkali and rare-earth elements and type of structure will take into account to reveal the influence on the heat capacity of layered oxides [3-5]. It will be shown the opportunity to predict the thermodynamic properties by the application of the additivity principle of heat capacity for layered compounds built of fragments of various structural types.

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WHY IS IT IMPORTANT TO COMPLEMENT EXPERIMENTS WITH COMPUTATIONAL METHODS FOR MOLECULAR CRYSTALS: CRYSTAL STRUCTURES, THERMODYNAMIC AND MECHANICAL PROPERTIES OF VARIOUS POLYMORPHS

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Polymorphism is a widespread phenomenon for organic molecular crystals. Different crystal structures determine the distinction in physicochemical properties, such as the shelf-life stability, solubility, bioavailability, tableting, etc. These properties are crucial for pharmaceutics, where polymorph screening is an almost mandatory procedure during drug discovery and development. Another key area for molecular crystals is high-energy materials, (e.g. explosives, pyrotechnic compositions, propellants, fuels) where thermodynamic stability, mechanical properties and stability are of great importance. All these properties are usually studied using mainly experimental techniques [1].

Nevertheless, computational methods may not only supplement experiments, but also replace laboratory research and development for large-scale projects using high-throughput simulations. Remembering previous 23rd RCCT conference sessions, professional community pointed out another emerging issue - creation and verification of thermodynamic databases, finding outliers and mistakes. This may become one of the most significant tasks in the field, taking account needs of verified databases for artificial intelligence (AI) and machine learning (ML) algorithms for predicting new materials and their properties [2]. Such corruption of databases may be deliberate or accidental, but anyway threaten future development in the area.

In this work we show perspective of various application of computational methods, including Force Field (FF), Semiempirical (SE) and DFT, for current and future works, based on worldwide and personal experience and vision. In addition to broad review of current computational methods, their advances and limitations, regarding thermodynamic, materials sciences and physical chemistry, specific examples of misleading experiments and measured properties are provided. It is shown, how mistakes in crystal structure solution may be found and checked in CCDC crystallographic database. Another option is restoring order in thermodynamic and structural stability of polymorphs which may coexist in different conditions using DFT calculations [4]. Finally, we suggest several techniques to model mechanical properties of molecular crystals which may exhibit an outstanding plastic, elastic and shearing behavior under stress.

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ORAL PRESENTATIONS

ON SOME SPECIFIC FEATURES OF SELF-ASSEMBLY OF AMPHIPHILIC HOMOPOLYMERS

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The amphiphilic homopolymers are macromolecules with monomer units composed of significantly different (hydrophobic and hydrophilic) groups and, thus, they are amphiphilic at the level of a individual monomers and possess the effective surface activity.

Amphiphilicity at the level of single monomer unit underlies the solubility of protein globules, the formation of collagen-like aggregates, the self-organization of thin fibrils from several intertwined macromolecules, and the association of fibrils into thick bundles-aggregates and fibrillar gels.

A specific feature of amphiphilic homopolymers is that the self-organization is determined not only by the presence of groups with different affinities for the solvent, but also by their relative position in the monomer units [1-7]. In some cases, this leads to the emergence of a specific entropy-driven attraction.

Taking into account this specific entropy-driven attraction is necessary when creating complex functional systems with properties changed on demand.

The report will review some of these systems [1-7], present the results of our computer simulations, original theoretical descriptions and comparisons with literature experimental data.

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WATER PURITY CONTROL: RESEARCH OF NANOSCALE IMPURITIES AND EVALUATION OF WATER PURIFICATION METHODS USING ULTRAMICROSCOPY

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Water is an indispensable resource crucial for sustaining life and driving human progress. Its purity is pivotal in safeguarding human health, preserving ecosystems, and bolstering industrial processes. Ensuring water purity is of paramount importance in scientific research, particularly in areas where observed effects are nuanced and demand highly sensitive research methods, as well as in the synthesis of nanoparticles and studies of crystallization processes.

In laboratory settings, specialized water purification systems are capable of producing Type I water purity, characterized by high resistivity (no less than 18 MΩ·cm), a parameter controlled through experimentation. However, the control over the presence of nanoscale impurities in the obtained water is often lacking, and water considered pure based on parameters such as conductivity may indeed contains a significant amount of nanoscale impurities.

Ultramicroscopy [1] and the NP Counter device (NP VISION, Russia), based on this method, enable the visualization of individual particles in liquid with sizes as small as 10-20 nm, while specialized software facilitates particle counting and concentration determination in the sample.

The study empirically demonstrates that water corresponding to Type I water conductivity, obtained using reverse osmosis water purification devices, may contain up to 10^7 particles/ml of nanoscale impurities, depending on the condition of the filter system.

The efficiency of water purification using syringe filters of 0.45 µm, 0.22 µm, and 0.1 µm was investigated. Measurements of the numerical concentration of nanoscale impurities in water were conducted using ultramicroscopy after several cycles of water filtration through syringe filters.

Ultrasonic (US) dispersion is employed for sample homogenization in laboratory conditions. Due to cavitation effects, particles from the material of the ultrasonic probe submerged in the sample, and particles from the vessel walls where dispersion occurs may infiltrate the sample. The study illustrates, utilizing dynamic light scattering and ultramicroscopy, the variations in average particle size and their concentration in the water sample over time under the influence of US dispersion.

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COMPARISON OF THE CAPABILITIES OF DSC AND THE OPTICAL METHOD FOR STUDYING THE PHASE BEHAVIOR OF NANO-SIZED AQUEOUS DISPERSIONS OF N-ALKANES

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Phase Change Materials (PCM) are materials that utilize the latent heat of their phase transitions during operation. Thermal energy is stored during melting, and released during crystallization. Interest in the physicochemical properties of materials, which can serve as the basis for PCM development, is growing every year.

Studying the phase behavior of n-alkanes is intriguing both from a fundamental perspective and as an applied task in PCM development. It is important to note that n-alkanes exhibit peculiarities in their phase behavior: rotational phases (quasicrystalline structures) and the surface crystallization effect. Investigating such systems under confined geometry conditions is relevant.

n-Alkanes are considered a promising basis for PCM creation due to their wide range of temperature intervals for phase transitions depending on the number of carbon atoms in the molecule, relatively high heat capacity, non-toxicity, chemical inertness, and cost-effectiveness.

This study focuses on investigating the physicochemical properties of a series of samples of nano-sized aqueous dispersions of n-alkanes (from $C_{18}H_{38}$ to $C_{22}H_{46}$) obtained through ultrasonic dispersion without the addition of surfactants. The characteristic particle size (radius) in such dispersions is 100 nm. Both an original optical method and differential scanning calorimetry (DSC) were used to study the phase behaviour of n-alkane particles in these systems. It has been shown that for low-concentration dispersions, the sensitivity of the micro-DSC method is inferior to the optical method in detecting temperatures of phase transitions.

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CONCENTRATIONAL TETRAHEDRON OF Li-Mn-Eu-O SYSTEM

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Using the method of topological modelling and based on fragmentary experimental data [1-3], an isothermal concentrational tetrahedron of the Li–Mn–Eu–O system was plotted [4] for the first time, describing possible solid-phase transformations in the system that occur at a constant temperature with a change in partial pressure of oxygen PO_2. The polymorphism, solid solutions formation, Li-/O-nonstoichiometry as well as metastable phases/equilibria have been neglected. The tetrahedron is being divided into 36 trigonal bipyramids. Rising up from the base (Li–Mn–Eu triangle, Figure) to the top vertex of the tetrahedron (O) corresponds to a change in phase equilibria in the Li–Mn–Eu–O system with increasing partial oxygen pressure. At a fixed Li : Mn : Eu ratio, isoconcentrates successively pass through different triangular pyramids of the Li–Mn–Eu–O isothermal tetrahedron, Fig. 1, and the phase composition of the composites changes with PO_2 varying. The diagram ($T <$ 267 K) covers the PO_2 range of 10^{-10}–10^{15} Pa, considering calculated Mn–O diagrams *(P–T)*. At PO_2 close to 21 kPa spinel $LiMn_2O_4$ forms thermodynamically stable composites with Li_2MnO_3, $EuMnO_3$, $EuMn_2O_5$, Mn_3O_4 and Mn_2O_3. Apparently, excess oxygen pressure will lead to the formation of $LiMn_2O_4$ composites with MnO_2 and MnO_3.

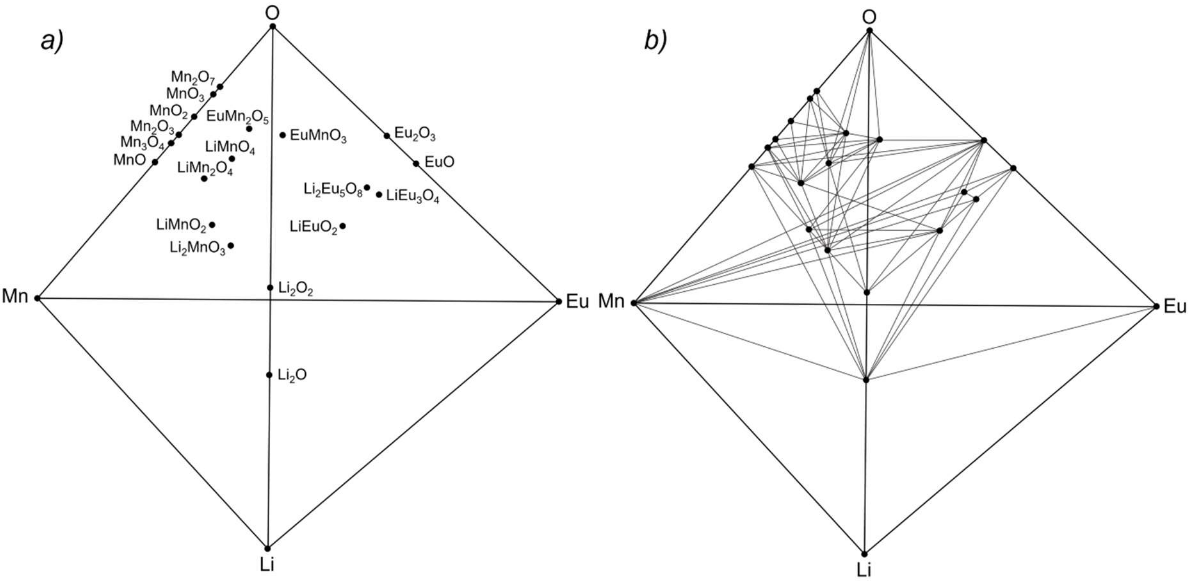

Figure. Isorthermal concentrational diagram of subsolidus phase equilibria in the Li-Mn-Eu-O system: *a*- figurative points, *b*- tetrangulation.

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PREDICTING SHEAR VISCOSITIES OF BINARY ORGANIC MIXTURES BY MOLECULAR DYNAMICS METHODS

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This report is devoted to our participation in the 12th Industrial Fluid Properties Simulation Challenge. During this Challenge, we use the atomistic modeling methods [1] for the blind prediction of the concentration-viscosity dependencies of organic mixtures at 298.15 K and 1 bar. Two mixtures are considered: tributyrin+1-decanol and 1,2-butanediol+1-decanol. The interatomic interactions are described using the COMPASS class II force field, which is modified for the reproduction of the viscosities of pure compounds. The Green-Kubo method is used to calculate the shear viscosities. The time decomposition method is applied for the accurate calculation of the Green-Kubo integral limit. Our approach accurately reproduces the shear viscosities of pure tributyrin, 1-decanol and 1,2-butanediol, and provides predictions for the viscosities of mixtures (see Figure 1). The relative mean absolute error between the predicted and experimental values does not exceed 10 %.

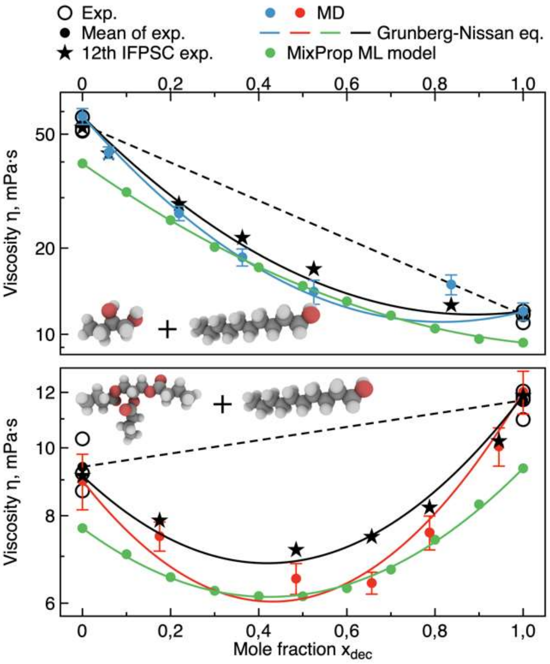

Figure 1. The predicted shear viscosity dependencies on concentration for tributyrin+1-decanol and 1,2-butanediol+1-decanol. The solid red and blue curves are their fits using the Grunberg-Nissan equation. The black circles show available experimental data for the pure compounds, while the black points denote their averages. The green points show the values calculated using the MixProp ML model.

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The work is supported by the strategic academic leadership program “Priority 2030” (Agreement 075-02-2021- 1316 30.09.2021).

THERMAL ANALYSIS AT THE BASIS OF DEVELOPMENT OF METAL FUEL

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Thermal analysis is based on the automatic recording of heating (cooling) curves in time-temperature coordinates, developed and presented by N.S. Kurnakov at the beginning of the last century (1904). Later, differential thermal analysis and scanning calorimetry appeared, allowing one to obtain information about the thermal effects of exo- and endothermic processes in controlled gaseous environments. In combination with the simultaneous recording of changes in the mass of the sample and the composition of the gaseous medium at the outlet of the reaction volume, the experimental capabilities and scope of thermal analysis have significantly expanded. This became especially evident with the advent of the possibility of phase analysis directly during heating of samples of the metals under study.

In this report, using the example of the search for new metallic fuels with increased reactivity, the capabilities of modern methods of thermal analysis are demonstrated. In combination with thermogravimetry and in situ differential scanning calorimetry, studies of the diffraction pattern of oxidation using synchrotron analysis allow us to draw conclusions about possible interaction mechanisms and develop the physicochemical basis for the creation of new functional materials.

As an example, in Figure 1 presents the results of such studies.

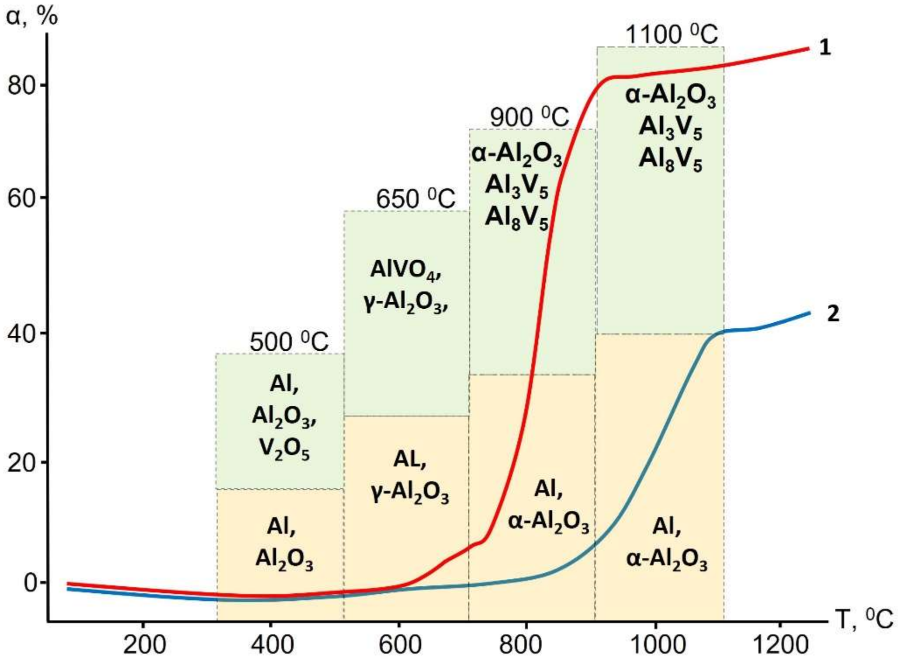

Figure 1. Results of studying oxidation powders (1 - ASD-4+$V_2O_5 \cdot nH_2O$; 2 – initial ASD-4) by thermogravimetry and diffraction methods using SR

The work was carried out in according with the state assignment of the Institute of Solid State Chemistry UB RAS № 124020600007-8.

INTERACTION OF GOLD(III) WITH SERUM ALBUMINS AND DNA IN AQUEOUS SOLUTION

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Interaction of metals with serum albumins is of special interest as it may mediate the toxic or beneficial action of metal ions and their metal complexes that are often considered (pro)drugs. Among metals, gold(III) draws special attention because its complexes resemble cisplatin and other similar platinum(II) complexes in structure and electron properties. Due to this similarity, the coordination compounds formed by gold(III) can find application in medicine as antitumor and antibacterial agents. The complexes are considered to bind with DNA, disrupting its normal replication. However, there are a few available papers devoted to the study of the interaction between tetrachloroaurate(III), which is used often for the synthesis of other gold(III) complexes, and DNA, while no one reported any data on the gold(III) complexation with proteins. The stability constants of gold(III) and DNA or albumins (transport molecules presenting major share of all proteins in blood) are also useful for studying the reactions between gold(III) complexes and DNA or albumins, as the dissociation of the metal complex is possible.

Tetrachloroaurate(III) hydrolysis, protein self-association and interactions involving chloride ions are accounted for to determine the most probable stoichiometric composition of gold(III) associated with proteins and the binding constants (Table 1).

Table 1. Equilibrium constants of the gold(III) species binding to bovine and human serum albumins at T = 298.2 K, p = 0.1 MPa

Gold(III) species	Medium	BSA		HSA	
		M to protein ratio	lg K’ per 1 gold(III) complex	M to protein ratio	lg K’ per 1 gold(III) complex
$[AuCl_4]^-$	0.1 M NaCl	20±5 : 1	4.2±0.5	20±5 : 1	3.9±0.1
$[AuCl_3OH]^-$	No NaCl	6±1 : 1	5.1±0.5	3±0.3 : 1	3.6±0.3
$[AuCl_2(OH)_2]^-$	No NaCl	4±1 : 1	4.9±0.5	2±0.3 : 1	3.8±0.3

In addition, this report will describe the interactions between $[AuCl_4]^-$ and its hydrolyzed species and DNA in pure water and aqueous 0.1 M NaCl solution. Binding mode and binding constants of gold(III) species to DNA are determined from the results of UV-Vis and circular dichroism titration, while the kinetic fluorescent measurements are used to study the ethidium bromide replacement. Atomic force microscopy is also used to show the influence of gold(III) species on DNA. The data obtained are used to calculate the equilibrium composition of the solution containing $[AuCl_4]^-$, biologically active hydrazone derived from pyridoxal 5’-phosphate and serum albumin and DNA at different pH values.

Moreover, a brief discussion of the inhibiting action of gold(III) species on alkaline phosphatase from the bovine intestinal mucosa will follow.

The financial support of Russian Science Foundation is greatly appreciated (project number grant number 22-73-10009, https://rscf.ru/project/22-73-10009/.)

INVESTIGATION OF THE POSSIBILITY OF FORMING OF LOW-MELTING HIGH-ENTROPY ALLOYS

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Currently, high-entropy alloys (HEAs) are of great interest to researchers due to their properties, in particular, high hardness, wear resistance, corrosion resistance, and resistance to ionizing radiation [1-3]. A large amount of research is associated to the study of of HEAs based on 3d transition elements, refractory, rare earth, light metals, high-entropy metal glasses, ceramic HEAs in the form of oxides, carbides, borides, nitrides. A separate group includes alloys containing elements with a low melting point (Bi, Ga, Pb, Al, Sn, Zn, In, Sb, and others), in which fatigue resistance, plasticity, and adhesion to other metallic materials play an important role [4].

It is necessary to noted that low-melting HEAs are not well investigated. Therefore, the purpose of this work was to study the possibility of forming a HEAs based on Al, Zn, Bi, Pb, Sn, In, Ga, Sb, and so on.

As the software to predict the phase formation, crystal lattice and microstructure of a solid solution, mechanical properties of HEAs the program HEAPS was used [5]. Calculations and evaluation of 30 physical and semi-empirical parameters and 19 criteria for 56 variants of five-component alloys of equimolar composition, which can be formed from the above elements, were carried out.

It is shown that only the AlGaZnSnSb alloy is a single-phase solid solution, for the other compositions the formation of multiphase solid solutions, intermetallic compounds and bulk amorphous metallic glasses is possible.

Thus, the performed calculations allow us to identify potentially high-entropy alloys. However, it should be noted that the approach used is evaluative. To reveal the full picture, it is necessary to conduct comprehensive complex studies, including quantum mechanical calculations of the crystalline and electronic structure of alloys, computer modeling of processes in HEAs by molecular dynamics methods, as well as thermodynamic calculations, which will allow us to obtain temperature dependences of the equilibrium phase composition and thermodynamic characteristics of the investigated systems.

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CALCULATION OF GERMANE ISOTOPOLOGUES THERMODYNAMIC FUNCTIONS FROM HIGH-RESOLUTION IR SPECTRA

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Interest in the study of germane isotopologues is due to the development of a hydride method for high-purity isotopically enriched germanium preparation. This material is promising for making the quantum computing devices and detectors of neutrinoless double beta decay. The most important fundamental properties of substances are their thermodynamic functions. They determine the stability of compounds under various conditions and make it possible to calculate the equilibrium concentrations of components in chemical systems with these compounds. To calculate the thermodynamic functions of gases, the method of statistical thermodynamics, based on the calculation of partition function of molecules, is most often used. The information for calculations is the data from the vibration-rotation spectra. Statistical calculation has great practical importance, since direct experimental measurement of thermodynamic properties of gases is usually difficult and laborious.

The objects of study were isotopically enriched germanes with an enrichment degree of 99.9 vol. %. The samples were synthesized using the “chloride” method, purified by the rectification and then enriched with the isotopes ^{72}Ge, ^{73}Ge, ^{74}Ge and ^{76}Ge by the centrifugal method at Joint Stock Company “Production Association Electrochemical Plant” (Zelenogorsk, Russia). Rotation-vibration spectra with a resolution of 0.003 cm^{-1} of isotopically enriched germane samples were recorded using Fourier transform infrared spectroscopy. Standard thermodynamic functions of germane isotopologues ^{70}GeH$_4$, ^{72}GeH$_4$, ^{73}GeH$_4$, ^{74}GeH$_4$, and ^{76}GeH$_4$ are calculated in "harmonic oscillator – rigid rotator" and "anharmonic oscillator – oscillating non-rigid rotator" (AOONR) approximations and by the combining the experimental energy values with the "AOONR" approximation. The standard heat capacity, entropy, enthalpy of heating and the reduced isobaric-isothermal potential were calculated. For germane ^{76}GeH$_4$ these values amounted to $S^o(298.15)$ = 217.656(2) J/(mol·K), C_p^o (298.15) = 45.133(2) J/(mol·K), $\left(H^o(298.15) - H^o(0)\right)/RT$ = 4.33785(2), $\Phi^o(298.15)$= 181.5889(2) Дж/(мол.·K). The influence of the isotope effect on the values of thermodynamic functions at 298.15 K is 0.164 J/(mol·K)/a.m.u. for the entropy and reduced isobaric-isothermal potential; 0.003 J/(mol·K)/a.m.u. for the heat capacity and 0.3 a.m.u^{-1} for the reduced enthalpy of heating. Approximation coefficients were calculated to find the values of the germane isotopologue thermodynamic functions in the temperature range 200–700 K. Influence of the isotope effect on the value of the thermal decomposition standard equilibrium constant of germane was estimated to be 2 %/a.m.u. The equilibrium interatomic distance r_e(Ge–H) in the germane molecule, independent of the mass of the isotope, was determined as 1.51710(2) Å. Limiting requirements were formulated for accurate determining the rotational constant and the central position of the bands in order to detect the influence of the isotope effect on the thermodynamic functions and interatomic distances of germane isotopologues. It was found the uncertainties of the central frequencies and rotational constant should be lower than 2×10^{-3} cm^{-1} and 2×10^{-2} cm^{-1}, respectively.

ELECTROCHEMICAL CHARACTERISTICS OF $LiAsF_6$ SOLUTIONS IN PROPYLENE CARBONATE – DIMETHYLSULFOXIDE BINARY MIXTURES

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The creation of experimental database on the physicochemical properties of electrolytes is important for the development of solution theory and the development of lithium chemical current sources.

In this work, the electrical conductivity of an electrolyte system containing lithium hexafluorosenate in a mixed solvent of propylene carbonate (PC) - dimethylsulfoxide (DMSO) in the temperature range from 253.15 to 333.15 K. The rise of temperature leads to increasing of the specific electrical conductivity in the studied region of ionophore concentrations range over the entire PC–DMSO mixture composition range. The use of mixed solvent PC – DMSO allowed increasing the $LiAsF_6$ solution conductivity compared to solutions of this ionophore in PC. The obtained results suggest that in the studied solutions the process of charge transfer in the studied region of ionophore concentrations is carried out according to the ion-migration mechanism. A quasi-crystalline model of electrolyte solution [1] was applied to the investigated systems, according to which ions can occupy positions corresponding to the positions of ions in an ionic quasicrystalline lattice, distorted as a result of the interaction of ions with solvent molecules. For all investigated systems the activation energy ($E^{\neq}$) of the charge transfer process linearly depends on the concentration of the ionophore in the solution according to the equation:

$$E^{\neq} = E^{\neq}_0 + x_2 \cdot E^{\neq}_{el},$$

where $E^{\neq}_0$ is the solvent contribution into the ionic conductance activation energy;
$E^{\neq}_{el}$ is the ionophore contribution into the ionic conductance activation energy;
x_2 is the mole fraction of the dissolved substance.

The process of charge transfer in the investigated system is mainly determined by the viscosity of the solvent.

It was found that solutions of $LiAsF_6$ in a mixed solvent PC-DMSO have a narrower electrochemical window compared to solutions of this ionophore in PC and DMSO, which is due to a shift in the cathodic decomposition potentials to the positive region. It is assumed that in a mixed solvent, solvate complexes of lithium ions are formed with a mixed shell containing simultaneously molecules of propylene carbonate and dimethylsulfoxide, which have reduction potentials higher than solvate complexes of lithium ions in individual solvents. In the anodic region, changing the composition of the mixed solvent and the local environment of the anion does not complicate the oxidation of the electrolyte solution [2].

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4D STRUCTURE-PROPERTY STUDIES OF NATIVE CYCLODEXTRINS

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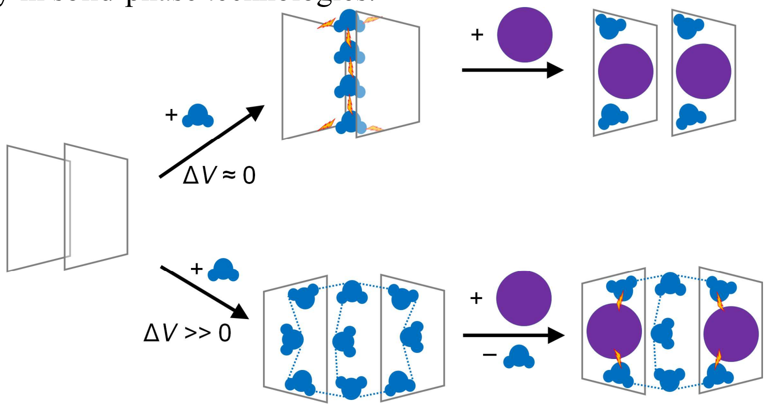
Significant number of cyclodextrin (CD) applications has solid-phase dosage forms: powders, tablets, capsules. The development and optimization of such applications require accurate knowledge of the structure of dry cyclodextrins. Crystallographic analysis can provide only structures of the hydrated CDs, while as the intermediate hydrates and dry CDs remain in a grey area. Our study is focused on the structural features of dry cyclodextrins, what reveals the role of water in guest inclusion and new approaches how to increase the inclusion capacity in solid-phase technologies.



Effect of water's energy on guest inclusion by cyclodextrins.

The role of water during CD complexation can be explained by the density of crystal packing of CD hydrates. For this study, we performed the powder XRD indexation of unit cell parameters for all natural CDs and their intermediate hydrates. These structural data are also in good agreement with melting parameters of natural CDs using fast scanning calorimetry (FSC).

FSC is state-of-the-art method which allowed to find the melting points [1] and enthalpies for the natural CDs. The obtaining of such data is possible due to extremely high heating rates up to 2.4 million K/min, opening access to study new processes which were 'hidden' by time in conventional methods of analysis. Such data are essential for understanding structure-property relationships.

The phase-temperature study of β-cyclodextrin revealed the new energy-rich polymorph III [2]. The dissolution of polymorph III in liquid water is 4.3 and 2.3 times faster than dissolution of polymorph I and hydroxypropyl-β-cyclodextrin (HPβCD), respectively, under the same conditions. Polymorph III dissolves in water vapors at the same humidity as the highly water-soluble HPβCD and has a higher affinity for water with a more negative hydration Gibbs energy than polymorph I. Thus, the new polymorph can be used for preparation of inclusion compounds in pastes or for a quick removal of undesirable compounds from water being a cheaper alternative to the chemically modified β-cyclodextrin.

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DENDRIMERIC AZOMETHINE Fe^{3+} COORDINATION COMPOUNDS CONTAINING CARBAZOLE UNITS

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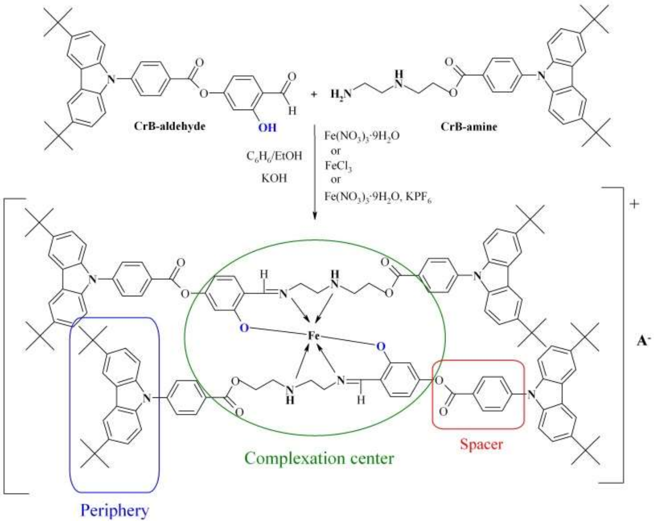
A new of azomethine Fe^{3+} complexes containing photoactive fragments at the periphery of the ligand were synthesized according to Scheme 1. All spectral characteristics of starting compounds (**CrB-aldehyde** and **CrB-amine**) are presented recently [1].

The fluorescence quantum yield ranges from 20 to 71% and depends on the nature of the counter-ion. It should be noted that the metal atom does not lead to fluorescence quenching. The fluorescence lifetime (τ_F) of the complexes in dichloromethane solution is 9.9, 10.1, 9.8 ns for **I-III**, respectively. The nature of the counter-ion does not affect τ_F value.



Scheme 1. Synthesis of iron(III) coordination compounds, where A^- is NO_3^- (I), Cl^- (II), PF_6^- (III).

The magnetic properties of the studied complexes were investigated by two methods: SQUID magnetometry and EPR spectroscopy. Magnetic measurements revealed that all compounds are in mixed low-spin (LS, S = 1/2) and high-spin (HS, S = 5/2) states: at room temperature compound **I** contains 49.4% LS and 50.6% HS Fe(III) ions, compound **II** - 78.6/21.4 % and compound **III** - 71.4/28.6 %, respectively. All compounds exhibit antiferromagnetic exchange interactions between neighboring Fe(III) ions. We believe that the presence of fragmented spin chains in the structure leads to the appearance of such AFM interactions due to the π-π stacking of benzene rings. EPR measurements confirmed the presence of HS states of Fe(III) ions and made it possible to distinguish two types of them - with strong low-symmetry and weak distorted octahedral crystal fields. The EPR signal from LS centers is not visible due to its broadening as a result of dipole-dipole interactions and superposition on the signal from I-type HS centers. The signal from Fe(III) centers with weakly distorted octahedral crystal fields has a similar characteristic to that of the ferromagnetic resonance line.

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ABRUPT BEHAVIOR OF THE P-T AND C_V-T ISOCHORES TO PRECISELY MEASUREMENT OF THE PHASE TRANSITION AND CRITICAL PROPERTIES OF THE COMPLEX THERMODYNAMIC SYSTEMS

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Various criteria, for example, sharp discontinuity of the measured properties occurring at the liquid-gas phase transition point, discontinuity of the heat capacity, ultrasonic wave attenuation, or abnormal enthalpy changes, have been used by various authors to determine the liquid-gas phase transition points in different type experiments. In the present work we used isochoric *P-T* breakpoint and isochoric heat capacity jumpwise behaviour in pure and complex multicomponent thermodynamic systems to precisely determine the liquid-gas phase transition parameters (T_S,P_S,ρ_S) and the critical properties (T_c,P_c,ρ_c). All experiments were started in the two-phase (liquid+gas) region at constant density (isochore heating) and completed in the one-phase region, liquid or vapor depending on filling factor. Between the initial two-phase (liquid+gas) and the final single-phase (liquid or gas) states, the system undergoes a liquid+gas phase transitions (L+G⇒L or L+G⇒G depending on filling factor) at temperature T_S for each fixed density ρ. Therefore, this method enables one to determine the phase transition temperature T_S as an abrupt point where measuring properties exhibits discontinuity. For example, isochoric heat capacity $\Delta C_V = C_{V2} - C_{V1}$ or slope of the *P-T* isochore changes ($\Delta\gamma_V = \gamma_{V2} - \gamma_{V1}$, where γ is the thermal-pressure coefficient, $\gamma_V=(\partial P/\partial T)_V$). In the present work we used the method to accurately measure phase-transition and the critical properties of various systems (pure fluids, binary and ternary mixtures) in calorimetric (C_VVT) and volumetric (*PVT*) experiments. As an example, Figure 1 illustrates the experimental C_V-T and *P-T* dependence for biojet fuel components (methyl decanoate) along the selected isochores near the phase transition temperature. As one can see, at the phase transition temperature C_V and γ_V exhibit abrupt behavior which corresponds to the phase-transition temperature.

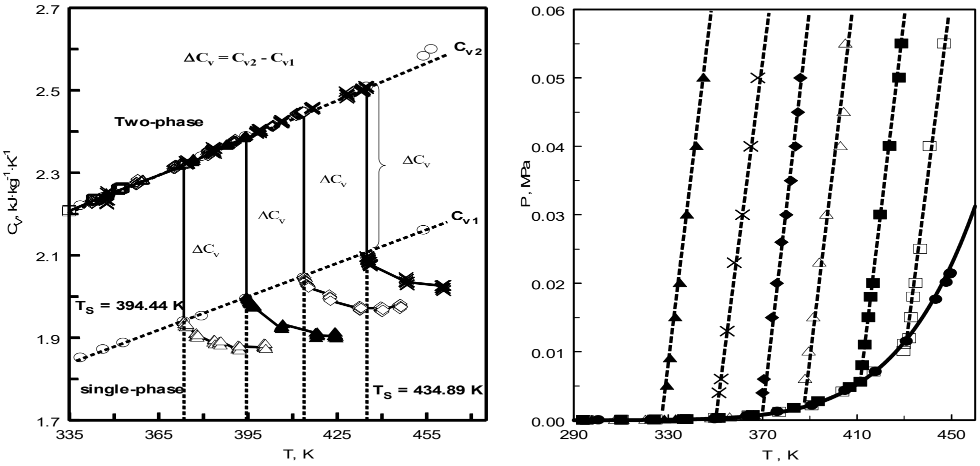

Figure 1. Temperature dependence of the isochoric heat capacity (left) and the pressure (right) of methyl decanoate along the selected isochores near the phase transition temperatures. Solid curve is the vapor pressure.

THERMODYNAMICS OF THE COMPLEXATION OF RUTIN WITH HYDROXYPROPYL-β-CYCLODEXTRIN

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Cyclodextrins (CDs) are cyclic oligosaccharides, formed by α-1,4-linked glucose units, with a hydrophilic outer surface and a lipophilic central cavity [1]. CDs can form inclusion complexes when the "guest" molecule, usually a drug, is partially or fully included inside the CD "host cavity". Owing to their hydrophobic cavity, cyclodextrins form inclusion complexes with a wide variety of hydrophobic compounds and change the physicochemical and biological properties of the guest molecules [2]. These changes may enhance the therapeutic potential of drugs by diminishing their decomposition, increasing solubility, and altering how they enter tissue. On the other hand, the solvent can also affect the bioavailability of drugs.

Natural plant-based compounds are nowadays of increased interest in the pharmaceutical field. Natural polyphenolic compounds have found their application in the treatment of neurodegenerative and cardiovascular diseases [3]. Many flavonoids, including rutin (Rut), possess antiviral [4], anti-inflammatory [5] and anticancer [6] activity. Rut, being a non-toxic and non-oxidisable molecule, offers a number of advantages when used in pharmaceuticals over similar flavonoids.

As most of the natural compounds, Rut is poorly solubility in water. Thus, its complexation with CDs can be helpful to overcome this issue. The solubilising CD properties can be also influence by the choice of solvent during molecular complex formation. In this regard, the studies of molecular complex formation between cyclodextrins and polyphenols in aqueous-organic solvents are of scientific and practical interest.

A thermodynamic study of complex formation between hydroxypropyl-β-cyclodextrin (HPβCD) with rutin in H_2O-EtOH solvents with various content of ethanol at $T = 298.15$ K was carried out. It was found that an increase in the concentration of EtOH in the solvent leads to a slight decrease in the stability of the complex and a marked decrease in the exothermicity of the reaction. Our findings indicate that the stability of [Rut HPβCD] is controlled by the enthalpy factor even with a decrease in the exothermicity of the complex formation.

Biodegradable nanoparticles (NPs) loaded with both bare Rut and [Rut HPβCD], coated with hyaluronic acid for active tumour targeting ability, were produced in this study. Indeed, [Rut HPβCD] inclusion complex was successfully obtained in ethanol, following an evaporation technique, paving the way for the development of NPs with a lower mean diameter, which is suitable for intravenously administered NPs intended for targeted cancer therapy. Furthermore, the negative surface charge attests to the effective coating of the NPs with hyaluronic acid.

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THERMODYNAMICS OF COMPLEX FORMATION OF NATIVE, MODIFIED, DIMERIC AND POLYMERIC CYCLODEXTRINS WITH THE IMMUNOMODULATOR BARICITINIB

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Baricitinib (BCN) is a new immunomodulator approved in 2017 for treating rheumatoid arthritis, which selectively inhibits Janus kinases and displays the anti-inflammatory, immunomodulatory, and antitumor properties. The BCN effectiveness is hindered by its poor aqueous solubility, leading to serious side effects. To address this issue, the solubilizers and drug delivery systems can be proposed and used.

In this work we enhanced the BCN solubility by means of inclusion complex formation with native, modified, dimeric and polymeric cyclodextrins (CDs, Fig. 1), which are oligosaccharides known for their ability to host-guest binding. We were aimed to reveal the influence of CD structure on the binding mode and thermodynamics of the inclusion complex formation with BCN.

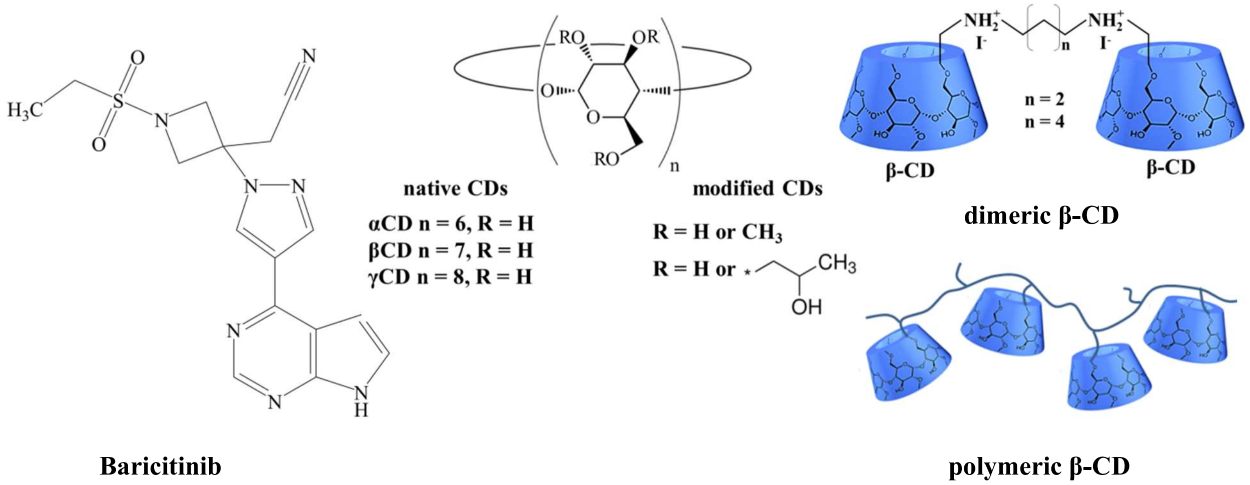

Figure 1. The structure of BCN and cyclodextrins under study.

The process of complex formation between BCN and CDs was studied using ^{1}H NMR, capillary electrophoresis, and solubility methods. Thermodynamic parameters of complex formation in buffer solutions (pH 1.6 and 6.8) simulating the gastrointestinal environment were obtained. The binding sites of BCN with CDs were determined. The influence of CD structure (size of the macrocyclic cavity, introduction of substituents, dimerization, and polymerization) and BCN ionization state on the thermodynamics of complex formation and solubilization efficiency was analyzed. The impact of CDs on the BCN permeability through the various model membranes (lipophilic PermeaPad and hydrophilic *SpectraPor*®) was also considered. It was demonstrated that the increase in BCN solubility in the presence of CDs is accompanied by a decrease in the membrane permeability of the drug. It was shown that concentration dependences of the permeability coefficient can be used to predict the binding constants of BCN with CDs and the solubility-permeability interplay.

MODELING OF PHASE EQUILIBRIA AND THERMODYNAMIC PROPERTIES OF PHASES IN WATER-SALT SYSTEMS CONTAINING METHANESULFONATE

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Methanesulfonic acid (CH_3SO_3H) is a strong acid, biodegradable stable under heating and during electrolysis, which makes it an attractive reagent for hydrometallurgy [1]. Methanesulfonic acid occurs in aerosols in atmosphere [1], making it a minor but important constituent of geological systems. Still, until recent, even the data on phase equilibria and thermodynamic properties in binary water-salt systems were absent.

We can group water-salt and water-acid-salt systems considered in this work in two categories. First is a number of systems that occur mostly in technogenic objects ($Me(CH_3SO_3)_2$-CH_3SO_3H-H_2O, Me = Cu, Zn, Ni, Co, Mn) which were mostly studied by our scientific group (eg., [2]) and which lacked any information on phase equilibria and thermodynamic properties. The other one is a set of systems that occur mostly in geological objects ($LiCH_3SO_3$-H_2O, $Me(CH_3SO_3)_2$- $M(CH_3SO_3)$-H_2O, Me = Ca or Mg, M = Na or K; KCH_3SO_3 - $NaCH_3SO_3$ -H_2O). In latter case a very fragmentary dataset existed for almost all binary systems, and a Pitzer model was fitted for binary solutions at 298.15 K for $M(CH_3SO_3)$-H_2O (M = Na, Li, K) [3].

Lacking experimental data (SLE – solid liquid equilibria, VLE – vapor-liquid equilibria, volume – volumetric properties) were obtained by following group of methods: (1) isothermal solubility, (2) differential scanning calorimetry, (3) static method of saturated vapor pressure, (4) dew point method for activity, (5) density measurements by oscillating U-tube apparatus.

For liquid phase, we chose Pitzer-Simonson-Clegg as primary model (and Pitzer model as a secondary one). It was parameterized using at least following types of data (a) VLE data, (b) SLE data for ice (binary systems), (c) SLE data for solids (as indirect data). For solid phase, we used temperature-depended solubility constants, optimized preferably from SLE in binary systems (in some cases, it was impossible, so a constant was optimized using SLE in ternary systems).

For the systems that occur mostly in technogenic objects and contain 3d-metal salts and acid, liquid model parameters obtained only from binary systems did not allow to reach satisfactory SLE and VLE prediction. Ternary parameters were calculated from experimental data, obtained in present work. For the systems that occur mostly in geological objects, and contain alkaline and/or alkaline earth methanesulfonates, parameters obtained only from binary systems allow to reach good VLE and more satisfactory SLE prediction.

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STUDY OF SPECTRAL, REFRACTIVE, MECHANICAL AND WETTING PROPERTIES OF GRAPHENE OXIDE CONTACTS FOR DISPLAY APPLICATIONS

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Classical liquid crystal display (LCD) schemes have a limitation on the electrical consumption of the optical devices due to the use of the orienting layers such as: lecithin, polyimide, fluoroplastic, etc. – to align the LC molecules. Significant part of the voltage falls on the orienting layer due to its high resistance, which leads to a decrease of the falling voltage on the LC layer. Graphene oxide (GrO) is a relatively young and unique material with promising applications in the field of the optical electronics. The possibility of the transition from the dielectric to the conductor state, high light transmission (in dielectric state) and hydrophilicity of the material[1,2] make it possible to obtain the thin contact films that capable of replacing the orienting layer in the classical LCD circuits of the display technology.

GrO has relatively high wettability (Contact angle is close to 25.3° at a drop of 3μl) and the solubility with the ethanol, toluene and isopropyl alcohol (IPA) solvents. Taking advantage of these properties, the graphene oxide solutions have been deposited by the spin coating on the glass and the ITO substrates. However, the experience shows that when the GrO film is reduced with solvents, the conductivity of the cell drops strongly changes due to the decrease in the density of the graphene flakes per unit of the surface area. In this regard, the "pure" graphene oxide was used for the experiments. The GrO used in this work is an original modification of the Hammers-Offeman method manufactured by NanoTechCentre Ltd (Tambov, Russia). The refraction of the GrO was measured in the IR spectral region for the unpolarized light at in the incidence angle of 45°.

The standard GrO has the following properties: the instability to water mixtures (which complicates its use in the LC structures), high transmittance of the film - on average 80-90% in the visible and IR ranges, and the IR-reflection of 7-10%. The lack of the conductivity is caused by the bonding of the carbon atoms with oxygen, giving the transition from sp2 to sp3 hybridization, the application of the film on the ITO substrate leads to its luminescence while maintaining high conductivity of the ITO.

The reduction of the graphene oxide is accomplished by heating the glass substrate to a temperature of 170°C or higher. At this temperature, a transition to a conductive state is observed. As the temperature increases, the resistance and reflectance of the film increases. The reduced GrO is more resistant to the active effect of the water mixtures. GrO has an IR-transmittance of 30-40% on average and the IR-reflection of 35-40%. The resistances of a 2 cm aperture cell vary from 20 kOhm, to 200 kOhm depending on the duration of the thermal exposure. The increased reflection of the film allows the structure to be used in the scheme of the nematic liquid crystals "on reflection" mode as a reflecting conducting electrode.

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THE METHODS OF CONTROL SURFACE FREE ENERGY IN LASER-ORIENTED DEPOSITED ITO THIN FILMS

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Indium tin oxide (ITO) is a semiconductor material with high optical transmittance in the visible spectral range, relatively small electrical sheet resistance, and competitive thermal and chemical stability. Due to these properties, ITO is a popular material for the transparent electrical contacts in optoelectronics. The current research was aimed at the problem of the control surface free energy (SFE, γ_S) of the ITO thin films. For the further comparison, the laser-oriented deposited ITO structures [1] with an average height in the range 90-110 nm were considered. The first method to modify the SFE was the electrical strength (E) varying during the deposition of the ITO layer. The next strategy for the SFE tuning was the deposition of the single-wall carbon nanotubes (SWCNTs) on the ITO surfaces with the various E as well. Finally, during the post-processing plasma treatment in an oxygen atmosphere with the various powers (P) of the generator was considered as an additional mechanism for the SFE change. The diagnostic of the SFE was performed via the contact angle (CA) measurements (OCA15EC, DataPhysics) with the distilled water, toluene and isopropyl alcohol (IPA) with the OWRK [2] method. The detailed procedure of the preparation and methodology of the measurements was described in paper [3]. The comparison of the SFE for the ITO modifications is demonstrated below.

Table. The comparison of the SFE of the ITO for the various modifications

Method of control	Mode	Contact angle, °			Surface free energy, mJ/m^2		
		Water	Toluene	IPA	Polar	Dispersive	Total
LOD of pure ITO	E=100 V/cm	85.4	7.3	X	8.2	22.2	30.4
LOD of CNTs on ITO	E=100 V/cm	115.7	24.9	X	0.8	29.2	30.0
	E=200 V/cm	95.7	22.7	X	1.3	25.0	26.3
	E=600 V/cm	119.5	19.1	X	1.8	31.4	33.2
Plasma treatment of ITO with CNTs (with various E)							
E=100 V/cm	P=10W (3 min)	72.8	X	7-10	14.9-15.1	16.2-16.3	31.2-31.4
	P=30W (3 min)	6.8	X	<5	9.7-9.8	67.1-67.2	76.8-76.9
E=200 V/cm	P=10W (3 min)	54.3	X	7-10	12.5-12.7	33.1-33.2	45.6-45.9
	P=30W (3 min)	4.8	X	<5	9.7	67.4-67.5	77.1-77.2
E=600 V/cm	P=10W (3 min)	70.9	X	7-10	14.7-14.8	17.8-17.9	32.5-32.7
	P=30W (3 min)	6.9	X	<5	9.7-9.8	67.0-67.2	76.7-77.0

According to the data shown in Table, it should be mentioned that the SFE of the ITO modifications could be tuned in the wide range. So, this feature of the ITO modifications in tandem with high performance of the electro-optical properties is quite relevant for the issues of the liquid crystal alignment, problems of the heterophase nucleation and for the microfluidic applications.

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THERMAL ANALYSIS OF NANOCRYSTALLINE POWDERS OF TRANSITION METAL CARBIDES

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Transition metal carbides possess high melting points and hardness, due to which they are the main components of refractory and hard ceramics, composite materials and hard alloys produced usually by powder metallurgy methods using high temperatures [1, 2]. One of the ways of improving the performance of carbide materials is a micro-to-nanostructure transfer [3]. However, the extremely large specific surface area of nanocrystalline powders of transition metal carbides increases their chemical activity and makes them very sensitive to impurities and heating [4].

In this work, simultaneous thermo-gravimetric analysis and differential scanning calorimetry (TGA-DSC) were used to study the behavior of micro- and nanocrystalline powders of nonstoichiometric carbides TaC_y, NbC_y and VC_y with a cubic structure (sp. gr. $Fm\text{-}3m$) and WC with a hexagonal structure (sp. gr. $P\text{-}6m2$) during heating in inert and oxidizing atmospheres. Nanocrystalline powders were obtained by high-energy milling of microcrystalline carbide powders in a planetary ball mill; their average particle size was varied from 50 to 10 nm by varying the duration of milling from 5 to 20 h. All the considered powders were certified using XRD, BET, SEM and chemical analysis for carbon and oxygen.

The study performed showed that, unlike microcrystalline powders, heating of nanocrystalline powders (TaC_y, NbC_y, VC_y and WC) in an inert atmosphere over the entire examined temperature range is accompanied by their decarburization as a result of the interaction of carbon with impurity oxygen. It was shown that an increase in the heating temperature of nanopowders is attended by the growth of their particles and enhanced decarburization, whereupon not only the composition of carbide (TaC_y, NbC_y, VC_y), but also the phase composition of powders changes. When heated to 1200°C and above, carbide nanopowders become microcrystalline. Heating of micro- and nanocrystalline powders (TaC_y, NbC_y, VC_y and WC) in an oxidizing atmosphere, regardless of particle size and non-stoichiometry y of carbide (TaC_y, NbC_y, VC_y), is followed by their oxidation and the formation of higher oxide (Ta_2O_5, Nb_2O_5, V_2O_5, WO_3). When the particle size of the powder is reduced, the oxidation onset temperature, the specific thermal effect and the mass gain of the sample decrease.

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APPLICATION OF PHYSICOCHEMICAL METHODS IN ANALYSIS OF COMPLEX CONNECTION OF Ag (I) WITH ACETYLCISTEINE

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In human, animal and plant organisms, amino acids play an important role in the biosynthesis of a number of compounds. The advantage of such preparations is that they are not foreign to the organism, so they are not toxic [1].

The purpose of the study. Synthesis, investigation, physicochemical and biological properties of complex compounds of Ag(I) with acetylcysteine by IR spectroscopic method.

Materials and methods of research. IR spectroscopic method was used to study the properties of complex compounds of Ag(I) with acetylcysteine.

The results of the study and their discussion. The IR spectroscopy is a fundamental method of investigating the structure of chemical compounds. The complex compound Ag (I) with acetylcysteine was identified by IR spectroscopy. The possibility and prospects of application of IR spectroscopy method for express diagnostics of authenticity of the studied complex compound Ag (I) with acetylcysteine have been investigated. In this work, the IR spectroscopy method was used to determine the structure of complex compounds of Ag (I) with acetylcysteine. On the basis of experimentally obtained data on absorption bands of functional groups it was suggested that amino-, sulphur- and carboxyl groups of acetylcysteine participate and in complexation with silver [2].

In order to assess the harmlessness of the compounds in an approximate therapeutic dose of 0,03 g/kg body weight with water orally (as a 10% suspension in physiological solution) were administered to white mice (weight 18 - 20 g, number of 5 pieces) and chinchilla rabbits (weight 2,5 – 2,7 kg, number of 5 pieces) 2 times a day for 7 days. The study on determination of toxicity of the new compound was carried out in three series of experiments on experimental rabbits of chinchilla breed (weight 2,0-2,5 kg n=6). As a result of experiments it was established that the maximum tolerated dose (MTD) of the obtained compound on rabbits is LD_{00}=3,0 g/kg, LD_{50}= 5,0 g/kg, LD_{100}=8,0 g/kg. The results of experiments showed that the developed compound is harmless and low toxic for laboratory animals [3].

High purity coordination compounds of Ag(I) with acetylcysteine have been synthesised. The composition, structure and properties of new coordination compounds of Ag (I) with acetylcysteine were established by IR spectroscopy. Harmlessness, acute and chronic toxicity of coordination compounds of Ag (I) with acetylcysteine were studied. The synthesised compounds were found to be low toxic.

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INTERMEDIATE STATES IN PROTEIN FOLDING: EXPERIMENTAL OBSERVATION AND THERMODYNAMIC CONSTRAINTS

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Despite the claims that the so-called Protein Folding Problem is solved, elucidating of the folding pathway and the associated energy surface of protein conformations is yet to be achieved.

Computer simulations show that during the process of protein folding many intermediate states can be populated, however, under native conditions the protein population is very homogeneous. Furthermore, the folding/unfolding equilibrium of many proteins is often well-described as a two-state transition, i.e., only native and unfolded states are populated at all conditions.

Hen-egg lysozyme is a classical model protein which is often presented as an example of a two-state folding. However, during the folding of lysozyme in water at least one intermediate state was detected [1]. Fast scanning calorimetry allows to probe the population of the non-equilibrium lysozyme states during the folding [2]. It shows a single intermediate that forms during the folding but is absent in the equilibrium population.

Equilibrium thermodynamics allows to put the constraints on the thermodynamic properties of intermediate states so that the transition appears to be a two-state one. The folding processes following these constraints must follow collapse and refinement model.

Based on the achieved data and the thermodynamic constraints the profile of the folding funnel can be inferred.

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EXPERIMENTAL ASSESSMENT OF THE PROPERTIES OF CRYSTAL NUCLEI IN THE SUPERCOOLED MELT

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Nucleation is a critical step of the crystallization process, yet the observation of the crystal nuclei and assessment of their properties remains a serious experimental challenge. This is due to their small size and transient nature.

Fast scanning calorimetry (FSC) proved to be an extremely productive method for studying nucleation and crystallization kinetics of various materials including polymers, alloys, and small organic molecules.

An approach for studying nuclei stability based on FSC was proposed [1]. The approach is a modification of the Tammann's nuclei development method, adding an intermediate heating step between nucleation and development segments. Additional heating step allows to probe the thermal stability of the nuclei. The latter itself is a function of the nuclei size. By using this technique, an estimate of the radial growth rate of nuclei can be achieved.

The determined growth rate of nuclei of poly-L-lactic acid (PLLA) is several orders of magnitude lower that the growth rate of crystals [2]. The approach was also used to investigate the thermal stability and the size of the crystal nuclei of small organic molecule tolbutamide. As in the case of PLLA, the radial growth rate of tolbutamide crystal nuclei is significantly lower that the crystal growth rate. At the same time, the nuclei of tolbutamide survive short heating even above the melting point of the crystals. We also show that the type of the crystal polymorph of tolbutamide is determined by the conditions of growth. The formation of the polymorph appears to be driven by the interplay between the kinetic and thermodynamic control, similar to the Ostwald's rule of stages.

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EQUILIBRIUM CONFORMATIONAL ENSEMBLES OF A MISFOLDING PEPTIDE UNDER VARIOUS CONDITIONS FROM ATOMISTIC SIMULATIONS

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A huge and biologically important group of proteins and peptides known as intrinsically disordered proteins (IDPs) lack a well-defined native spatial structure. Instead, they exist and play their functional role in a broad ensemble of rapidly fluctuating conformations corresponding to the shallow free energy minima. IDPs are linked to many severe diseases and represent prospective targets for innovative drugs. Interaction with other molecules in the environment of IDPs can lead to the shift of the conformational equilibria with the stabilization of certain conformers and changes in various properties.

One of the peculiarities of many IDPs is their ability to self-assemble into the long fibrillar structures consisting of beta sheets. Spontaneous aggregation of human beta-amyloid involved in Alzheimer’s disease is a well-known example. A seven-residue central fragment of beta-amyloid, KLVFFAE or Aβ16-22, is highly aggregation-prone on its own and is thought to act as a template for aggregation of the whole protein. Previous experimental studies have shown the ability of various denaturing agents to supress the amyloid aggregation of Aβ16-22 due to their influence on the conformational equilibria of the monomer.

The insights into the molecular mechanism of action of small molecules on IDPs require obtaining well-sampled ensembles of protein conformations in the absence and in the presence of these molecules. This will consume huge computational time even for short peptides if conventional molecular dynamics is used. In the present work, we apply an enhanced sampling technique, well-tempered parallel-bias metadynamics (WT-PBMetaD), which is based on on-the-fly construction of a time-dependent bias potential in the space of collective variables depending on the protein conformation. The bias penalizes the return to the previously visited points of this space.

We study the influence of common denaturants and osmolytes (urea, trimethylamine N-oxide and its mixture with urea, guanidinium chloride, trifluoroethanol) on the properties of the conformational ensemble of Aβ16-22. The results obtained using three different sets of collective variables and two different forcefields (CHARMM22* and AMBER99SB-ILDN) are shown to be in a good agreement with each other. The convergence and exploration of the phase space for simulations with different collective variables are also compared. Some of the experimentally observed effects of denaturants on the structure of Aβ16-22 are shown to be reproduced in simulations. The link between the conformational rearrangements of the peptide and the changes in its ability to aggregate in the presence of denaturants is discussed.

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THERMODYNAMIC STUDIES OF NON-CANONICAL NUCLEIC ACID STRUCTURES

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In the last decades, the discovery of non-canonical nucleic acid structures has shed light on a new role for DNA in biology. Recently, there has been growing interest in the study of non-canonical structures, i.e., G-quadruplex and i-motif, because of their possible involvement in many biological processes [1, 2].

In particular, non-canonical DNA structures may form *in vivo* in important genomic regions and intervene in several biological processes, including the modulation of oncogenes expression, and therefore represent potential anticancer drug targets [3] . For these reasons, in recent years, , there has been a growing interest in understanding more deeply the energetics of the conformational transitions of these structures with and without putative ligands [4,5].

Isothermal titration calorimetry (ITC) and Differential Scanning Calorimetry (DSC) have been proven to be a useful tool for studying the energetic aspects of non-canonical nucleic acid structures and their interaction with potential ligands. Particularly, calorimetric techniques have been applied many times to determine the thermodynamic properties of non-canonical DNA structures interactions to screening among various drugs and to address drug design [6,7]. Here, calorimetric methodologies, in combination with spectroscopic techniques, have been applied to study non-canonical DNA structures, and to obtain information about the energetics of these structures and their interaction with new putative drugs.

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SOL-GEL SYNTHESIS AND CHARACTERIZATION OF $10Gd_2O_3$-$90CeO_2$ (MOL.%) PRECURSORS AND CERAMICS

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Ceria-based ceramics are widely used as solid electrolytes in various electrochemical devices for renewable energy such, as solid oxide fuel cells. Such bottom-up manufacturing methods as sol-gel synthesis appear to be effective for the fabrication of ceramics with the fine structure. Thus, the goal of the research was to investigate of the effect of synthesis conditions on the phase compositions and structures of precursors and ceramics based on the gadolinia-doped ceria. For the object of the research $10Gd_2O_3$-$90CeO_2$ (mol.%) composition was chosen.

For this work, sol-gel synthesis in variation of the reverse co-precipitation has been chosen. 0.1 M isopropyl alcohol solutions of $Ce(NO_3)_3{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}6H_2O$ were added dropwise in 0.25 – 3 M isopropyl alcohol solutions of diethylamine (DEA) with the subsequent treatment (washing and drying at 298 or 393 K under pressure). During the synthesis, alkalic media and $T = 274–275$ K were kept. The received amorphous powders have been subjected to annealing at 573, 673, 773, 873, 973 and 1073 K for two hours. Precursors after synthesis and calcination investigated using the simultaneous thermal analysis (STA, 409 of C/4/G Jupiter, NETZSCH), the X-Ray Diffraction analysis (XRD, Bruker «D8-Advance», Cu-Ka the radiation, l=1.54 Å), the particle size distribution analysis (PSD, Horiba partica LA-950).

The content of cubic phase in the stabilized CeO_2 powders increased relative to amorphous phase with growth of calcination temperature. It was found that phase formation in $10Gd_2O_3$-$90CeO_2$ (mol.%) (10GDC) powders takes place according to Gd_2O_3–CeO_2 diagram. The increase of the DEA concentration from 0.5 up to 1 M barely cause effect on crystallization temperature, but leads to decrease of the average size of the agglomerates from 0.78 up to 0.13 μm. It has been established that a subsequent increase in the concentration of the precipitator up to 3 M increases the average size of the agglomerates. The use of isopropyl alcohol as a rinse for fresh precipitate of hydroxides and drying in air under pressure provides a significant decrease of crystallization temperature ~100 K and decrease of the average size of the agglomerates from 0.13 up to 0.10 μm. The increase of the temperature up to 573 K leads to one-order decrease of the average size of the agglomerates. At the last, CeO_2 powders obtained in optimized synthesis conditions were sintered into the ceramics with a fine structure, grain size ~ 0.2 μm and high relative density.

THERMODYNAMIC ASPECTS OF THE INTERACTION OF HYDROGEN WITH R_2FE_{17}

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The initial samples R_2Fe_{17} (R=Gd, Dy, Lu) were prepared as described in [1, 2] by melting stoichiometric mixture of charge 2-17 starting metals. The purity of the starting metals was above 99.9%. The characteristics of the initial samples and their hydrides were determined using X-ray phase analysis. XRD data showed that the initial R_2Fe_{17} samples were single-phase with a hexagonal structure of the Th_2Ni_{17} type (the $P6_3/mmc$ space group). The hydrogenation process did not change the structure of the initial samples, but only the expansion of the crystal lattice occurred. The initial samples were examined using a Tescan Vega 3 SEM scanning electron microscope (SEM), element mapping was carried out using an EDX prefix. The survey was carried out at HV=20 kW, WD=15 mm. The $R_2Fe_{17}H_X$ hydrides (R= Dy, Lu) were analyzed by particle size distribution using the CILAS 1180 Liquid laser particle size analyzer. The study of the interaction of hydrogen with R_2Fe_{17} was carried out by the Calvet calorimetry method at 200 and 250°C and hydrogen pressure up to 50 atmc using a Calve type calorimeter DAK-12. Dependencies P=f(C), ΔHabs.(des.) =f(C) and ΔSabs.(des.) =f(C) were obtained (P is the equilibrium pressure of hydrogen, ΔH is the enthalpy of the reaction, ΔS is the entropy of the reaction, C=H/ IMC). There is no plateau region on the dependence graphs P=f(C), however, on the graphs ΔHabs.(des.)=f(C) for R_2Fe_{17}-H_2 systems (R=Gd, Dy, Lu) there are regions where the values of ΔHabs.(des.) remain constant. It should be noted that the values of ΔHabs.(des.) change with changes in the reaction temperature, the hydrogen content in R_2Fe_{17}, and also decrease in absolute value during the transition from Gd_2Fe_{17} to Lu_2Fe_{17}, which is apparently due to the existing lanthanide contraction.

Hydrogen desorption from $R_2Fe_{17}H_X$ was also performed using a differential scanning calorimeter (DSC). Processing of DSC curves was carried out using NETZSCH Proteus and NETZSCH Kinetics Neo software. Three most common methods were chosen as non-converting non-mathematical methods of analysis: Friedman [3], Ozawa-Flynn-Wall [4] and Kissinger-Akahira-Sunose [5]. A superposition of peaks was observed on the DSC curves for Gd, and it was obvious that the process could not be described in one stage. The activation energy estimated by the three selected isoconversion methods varied from 100±15 to 150±15 kJ/mol with a conversion rate from 0 to 100%. Despite the fact that visually one peak was observed on the DSC curves for heavy elements (for example, Lu), and the activation energy varied less, from 90±15 to 110±15 kJ/mol with a degree of transformation from 0 to 100%, the model approximation in one stage is also a strong simplification of the process.

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LIPOPHILICITY AND SOLUBILITY OF 5-HYDROXY-6-METHYLURACIL AND ITS METHYL DERIVATIVES

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Study of lipophilicity and solubility is important for potentially biologically active compounds, in particular 5-hydroxy-6-metyluracil, which has a wide range of biological activity [1] and its methyl derivatives. For most derivatives of uracil, including 5-hydroxy-6-metyluracil, a problem arises with their bioavailability, since they have poor solubility in water and low lipophilicity. Therefore, the goal of this work was to determine the effect of methylation of the N^1-H, N^3-H and OH bonds of 5-hydroxy-6-methyluracil on the values of lipophilicity and solubility in water. The obtained values of lipophilicity and solubility in water of 5-hydroxy-6-methyluracil and its N- and O-methyl derivatives by shaking the flask in an octanol-water system and by HPLC are presented in the table 1.

Table 1 - Experimental values of lipophilicity and solubility in water of the studied compounds (pH = 7.4, T = 298 K)

Compound	Lipophilicity , LogP		Solubility, M
	Method of shaking the flask	HPLC	
5-hydroxy-6-metyluracil	-1.02 ± 0.10	-1.00 ± 0.10	0.013 ± 0.001
5-methoxy-6-metyluracil	-0.90 ± 0.14	-0.73 ± 0.06	0.089 ± 0.003
5-methoxy-3,6-dimetiluracil	-0.40 ± 0.06	-0.35 ± 0.06	0.029 ± 0.002
5-methoxy-1,3,6-trimetyluracil	-0.50 ± 0.01	0.11 ± 0.03	0.033 ± 0.001
5-hydroxy-1,3,6-trimetyluracil	-0.41 ± 0.04	-0.25 ± 0.04	0.053 ± 0.004

According to the data obtained, the least lipophilic and soluble in water is a 5-hydroxy-6-methyluracil and its methylation leads to an increase in lipophilicity and solubility. In the case of 5-methoxy-1,3,6-trimetyluracil, the values of lipofilic obtained by different methods are controversial. The best solubility is exhibited by 5-methoxy-6-methyluracil, which is the least lipophilic compound among the studied methyl derivatives of 5-hydroxy-6-methyluracil.

Thus, the methylation of 5-hydroxy-6-metyluracil leads to an increase in its bioavailability.

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THE DOPING OF $WB_{(5-x)}$ WITH TRANSITION METALS FOR CATALYTICAL APPLICATION

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Currently, the cost of many products is notably high due to the widespread use of catalysts made primarily of noble and rare earth metals for organic synthesis. Additionally, over 80% of the catalysts used in the domestic oil and chemical industries are imported, which can pose challenges in the current political climate.

Transition metal borides [1], [2] have been proposed as a cost-effective alternative to expensive catalysts. Tungsten borides have been investigated as potential catalysts for the hydrogen evolution reaction (HER) and the conversion of CO_2 to CH_4. They have also been suggested for use as catalysts in organic synthesis.

In our previous work, we demonstrated the effectiveness of higher tungsten boride (WB_{5-x}) in CO oxidation and photocatalytic CO_2 reduction reactions (both publications are in production). However, both reactions face energy barriers that must be overcome. One way to increase the catalyst's effectiveness is through doping with more active elements.

Due to the complicated structure of WB_{5-x}, molybdenum atoms with a radius similar to that of tungsten were proposed for doping. The material was then doped with Cr atoms, and Rh atoms were used to obtain reference data, as Rh is known for its catalytic activity.

Density functional theory (DFT) as implemented in the VASP package was used for all calculations. To avoid artificial interactions between periodic images of the slabs, a vacuum region of 25 Å perpendicular to each surface was employed. The doping atom replaced one tungsten atom from the surface layer of the (010) stable surface. At the starting point of relaxation CO, CO_2, NO, and O_2 molecules were placed 1.8 Å above the surface.

Based on the data obtained, the higher tungsten boride's ability to dissociate the O_2 molecule remains unchanged with doping, making it applicable for various oxidation reactions. Additionally, the adsorption energies of CO and NO molecules increase compared to those on pure WB_{5-x}. However, the most significant finding is that the doped samples show a reduction in the dissociation of CO_2 molecules, which was observed in pure WB_{5-x}.

Changes in electronic density and surface charges can determine the causes of unpredictable changes in adsorption energies and related energy barriers. Doped WB_{5-x} could be an alternative catalyst material for automotive motors due to its low adsorption energies of NO and CO molecules and relatively high adsorption energy of CO_2 molecule. As demonstrated in our previous study, WB_{5-x} is highly resistant to sulfur impurities in petrol, unlike traditional catalysts based on noble metals [3]. Additionally, WB_{5-x} surface facilitates the dissociation of the O_2 molecule without any energy barrier, making it a potential candidate for environmentally and industrially important reactions, such as ethylene epoxidation and hydrocarbon oxidation [4].

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DESCRIPTION OF INTERFACIAL BOUNDARIES AND AGGREGATES IN NONIONIC FLUIDS WITH THE AID OF MULTILAYER QUASICHEMICAL MODEL

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Interfacial properties are of key importance in many areas, including atmospheric phenomena, cosmetics, drug delivery, extraction of membrane proteins, oil recovery, etc. Thermodynamics of interfacial phenomena are well-developed [1]. Molecular theories have also been developed for nonuniform fluids that may contain similar-size or chainlike molecules. Nevertheless, these theories typically use average interaction parameters and do not distinguish between interactions of different functional groups in complex organic molecules. Thus, none of these theories may be applied for associating fluids, particularly for modeling hydrogen bonds. An exception is iSAFT (interfacial Statistical Associating Fluid Theory [2]), which describes the local properties of nonuniform systems with specific interactions. However, its application is rather involved computationally. In addition, the description of local orientations of functional groups is problematic within this theory, because the correlation function in the nonuniform system is obtained using the angle-averaged correlation functions of the uniform fluid. Thus, computer simulations – molecular dynamics (MD) and Monte Carlo (MC) – remain the major source of detailed structural information.

Recently formulated multilayer quasichemical model (MQuM) [3] takes into account specific interactions in fluid mixtures that contain chainlike and associating species. MQuM gives a particularly detailed information about the local structure of a nonuniform multicomponent fluid: the concentration profiles of monomeric molecules and of the constituent segments of molecular chains; the orientation profiles of chemical bonds in these chains and local orientations of pairs of contacting functional groups, including the hydrogen bonds. The MQuM is an extension – to flat and curved interfaces between fluid phases and mesoscale aggregates in solution – of the approach first proposed by Smirnova [4] for nonuniform solution near a flat solid wall.

In this work, MQuM model is applied to calculate the local structure, the pressure tensor and interfacial tension for micelles and reverse micelles in solutions, bubbles, drops, and flat interfacial boundaries in fluids that contain water, hydrophobic chainlike molecules (oil) and an amphiphilic component (surfactant). We compare our results with MD data and discuss the advantages and limitations of the model.

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DESIGN, CONSTRUCTION AND TESTING OF A NEW DUAL QCM BASED APPARATUS FOR THE DETERMINATION OF VAPORIZARION AND SUBLIMATION ENTHALPIES

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Quartz crystal-based microbalances (QCMs) have been used in microgravimetric techniques to measure the deposition of very small masses. This can be done as the increase in thickness of the "load" on the quartz crystal leads to a decrease in its resonance frequency. The first developments of this technique appeared in 1959 when Sauerbrey introduced this new mass measuring method [1].

A new dual apparatus for the determination of vaporization and sublimation enthalpies of low volatility samples based on QCM has been constructed. It has the capacity to make measurements under both Knudsen and Langmuir conditions. Although devices that have these conditions have been built and described in literature separately [2,3], to the best of our knowledge, no dual device has been presented. This new apparatus can be used to study several different types of samples (ionic or molecular organic substances in the condensed phases) over a wide temperature range.

Preliminary testing of the prototype has been carried out with several ionic liquids and molecular compounds that serve as benchmarks for phase change measurements. As such, this communication reports on the design, construction and testing of an experimental dual apparatus for the study of vaporization and/or sublimation of organic samples.

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CONFORMATIONAL ANALYSIS AS THE BASIS FOR THERMODYNAMIC CALCULATION

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The thermodynamic property calculation begins, as a rule, with conformational space definition within the lowest energy conformer is identified. For small and moderately complex molecules, the calculation can be restricted to the more stable conformer. However, when the number of atoms in molecule exceeds 20-30, the quantity of low–lying conformers (within 2 kcal/mol in energy) can be more than 10 and this has already a significant impact on many properties.

The number and energy of low-lying conformers are essential for the entropy and Gibbs free energy (as well as the related quantities) because the entropy and Gibbs free energy depend on the entropy of mixing and free energy of mixing, respectively. For 20-30 atomic molecules, these values may not be negligible that changes the predictive capabilities of the thermodynamic models.

The next (obligatory) step, after conformational space determination and allocating conformers according to their energies, is to search for the molar fractions and their temperature dependencies. The accurate determination of the molar fractions requires significant effort, as the "non-rigid" compounds are located in shallow energy wells on the potential energy surface. In this case, each molecule may have a large number of low-lying vibrational states that make a significant contribution to the vibrational part of the partition function. Processing of such states requires accounting for anharmonicity ("anharmonic oscillator").

We have recently studied a large number of cyclic and acyclic polyatomic compounds. The vibration contribution for the cyclic structures to the partition function was found using the second-order vibrational perturbation theory based on the Dunham series, with parameters obtained from two sets of frequencies (harmonic and experimental or harmonic and calculated anharmonic ones). The molar fraction calculations for compounds with internal rotations were performed using the Schrodinger torsion equation solution.

Conformational distributions for ibuprofen, oxocane, amino acids (cysteine and acetylcysteine), oxygen and nitrogen substituted benzenes, alkylthiophenes, and other compounds have been obtained. All rotamers were optimized by molecular mechanics with a valence force field UFF. The top 50 structures were further optimized by means of M06/DZP with the Slater Cartesian basis functions (6d 10f). Properties of structures falling within the range of up to 5 kJ/mol in total energy were calculated using the BMK, CAM-B3LYP, LC-wPBE, M06, wB97, wB97x functionals in the 6-311++G(3df,3pd) Gaussian spherical harmonics basis set (5d 7f).

The geometry, total electronic energy, harmonic and anharmonic vibrational frequencies of low-lying conformers are found. Potential and structural functions of internal rotation are obtained for most structures, and the Schrodinger torsion equations are solved in plane waves. The contributions of internal rotations are calculated taking into account the probability of location to a specific potential well on the potential energy surface. Based on the data obtained, the temperature dependences of molar fractions, entropy of mixing and free mixing energies, enthalpy of formation, and entropy and Gibbs free energy temperature dependences are calculated.

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DSC, DENSITY, ELECTRICAL RESISTIVITY AND MAGNETIC SUSCEPTIBILITY OF Al-Ni-Co-Cu-Zr HIGH-ENTROPY ALLOYS IN SOLID AND LIQUID STATES

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High entropy alloys (HEA) have attracted much attention nowadays. HEA with equiatomic ratio of initial components exhibit high values of mechanical properties, corrosion resistance, and unique electromagnetic properties, due to formation of single-phase (sometimes two-phase) solid solutions. Aluminium, 3-d transition metals (Co, Cu, Ni) and zirconium are the most common components in modern HEAs due to the ability of formation materials with low density compared with rare-earth high-entropy materials. In present work density, electrical resistivity and magnetic susceptibility of Al-Ni-Co-Cu-Zr HEAs were investigated experimentally for the first time in a wide temperature range, including liquid state.

Alloys of $Al_{20}Ni_{10}Co_{30}Cu_{30}Zr_{10}$, $Al_{30}Ni_{15}Co_{15}Cu_{35}Zr_5$ и $Al_{35}Ni_{10}Co_{15}Cu_{35}Zr_5$ compositions were prepared from pure elemental metals (> 99.99%) by the conventional arc-melting process under a flowing argon atmosphere. Differential scanning calorimetry (DSC) was used to determine the temperatures of structural phase transformations. The measurements were performed on a NETZSCH STA 409 PC thermal analyser. Density of the alloys was investigated by gamma-absorption method in the temperature range T = 300–1800 K at a heating/cooling rate of 2 K/min in helium atmosphere. Electrical resistivity of the alloys was studied by contact-less method in a rotating magnetic field and magnetic susceptibility was investigated by Faraday method in the temperature range T = 300–1800 K.

It was shown that alloys have a wide two-phase zone and solidus / liquidus temperatures, type of thermal reactions were determined based on DSC measurements. It was found that density polytherms of alloys have an almost linear form in solid and liquid states. The coefficient of thermal expansion and molar volume of alloys were calculated based on experimental data. Electrical resistivity and magnetic susceptibility curves have a more complicated form, in particular, section (500–750 K) where resistivity of the alloy decreases and magnetic susceptibility increases with increasing temperature was found.

Obtained results can be used as a basis for further work with high-entropy alloys of the AlNiCoCuZr system, and also for creation of new materials with good service properties.

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APPLICATION OF ATOMIC FORCE MICROSCOPY TO THE ENERGETIC MATERIALS SUBLIMATION STUDY

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Sublimation of energetic materials (EM) is a crucial process for fundamental research as well as for practical applications, especially for the EM detection. However, in the case of energetic materials the most of methods commonly applied for sublimation study (for example, thermal analysis) might be dangerous due to a high temperature heating required for the investigation. Currently, novel methods are being searched to study the EM sublimation safely. Previously the enthalpy of sublimation was shown to be acquired by atomic force microscopy (AFM) [1]. However, published data reveal that sublimation enthalpy measured by AFM is significantly affected by the experimental conditions, i.e., particle size and morphology, local environment and substrate material [2,3], which makes it difficult to interpret the results obtained.

We have studied the sublimation of pentaerythritol tetranitrate (PETN) microparticles in order to find the experimental conditions necessary for the correct assessment of the sublimation enthalpy using atomic force microscopy. The influence of microparticles morphology, substrate material, local pressure of AFM-probe and heating conditions is considered.

We have observed that at 45-60° the sublimation process of microparticles might be accompanied by the crystallization of amorphous PETN initiated by the local pressure of AFM-probe thus distorting the experimental results. We have found that for the correct estimation of the sublimation enthalpy by AFM the following experimental conditions are to be met: substrates with the low roughness and thermal conductivity (in particular, mica substrates), AFM probes with a low stiffness constant and a semi-contact mode, the analyzed microparticles are to be of height above 280 ± 30 nm. Finally, we have confirmed the advantages of AFM technique to obtain the sublimation enthalpy of the energetic materials, i.e., a very small sample masses (< 20 µg) and relatively low sublimation temperature, which reduces the risk of the uncontrolled combustion/explosion processes during heating.

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MODERN PREDICTIVE QUANTUM CHEMICAL CALCULATIONS FOR THERMOCHEMISTRY AND DECOMPOSITION KINETICS OF ENERGETIC MATERIALS

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Highly accurate theoretical values of bond energies and activation barriers of primary decomposition reactions are crucial for reliable predictions of thermal decomposition and detonation-related phenomena of energetic materials (EM). However, due to the prohibitive computational cost, high-level ab initio calculations had been impractical for a large number of important EMs of medium size, including, e.g., CL-20. The widely used DFT calculations very often could not provide the uniform “chemical accuracy” (~1 kcal/mol) and, ultimately, the convincing mechanistic evidence on the decomposition pathways of important EMs.

Here we report on the advantages in the theoretical thermochemistry and kinetics of EM achieved with the use novel local modifications of the coupled cluster (DLPNO-CCSD(T)). These render feasible high-accuracy calculations on caged polynitroamino and polynitro EMs, e.g., CL-20 and octanitrocubane (ONC). For all important species studied, the obtained values of bond energies are at least 10 kcal/mol more accurate than those reported in the literature so far. We also studied in detail the gas-phase thermochemistry of novel high-energy polynitro derivatives of 5/6/5 heterocyclic frameworks comprised of fused tetrazine and two triazole or pyrazole rings. To this end, we proposed and benchmarked a “bottom-up” approach. First, highly accurate multi-level procedures W2-F12 and/or W1-F12 in conjunction with the atomization energy approach were utilized for smaller species. In turn, for medium-sized species (up to 24 non-H atoms), these values were complemented with the enthalpies of isodesmic reactions calculated using DLPNO-CCSD(T)/aVQZ. In a more general sense, the latter approach is a viable step beyond the commonly used DFT procedures and represents a new level of predictive computational thermochemistry and kinetics for important EMs.

We also proposed a new approach for the determination of standard (solid) state enthalpy of formation of EM based on complementary high-level quantum chemical calculations (W1-F12 and W2-F12) of the gas-phase values and advanced thermal analysis techniques yielding sublimation enthalpies. We performed a massive benchmarking of the proposed procedure on a large set of EMs.

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VAPORIZATION BEHAVIOR AND THERMODYNAMIC PROPERTIES OF BaS AND $BaZrS_3$

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In the last decade, chalcogenide perovskites of general formula $MM'S_3$ (where typically M = Ba, Sr and M' = Zr, Hf) have attracted an ever-growing attention for their valuable optoelectronic properties [1] and have been proposed as a non-toxic and environmentally friendly alternative to hybrid lead halide perovskites as light harvesting materials in photovoltaic technologies. Indeed the latter, despite their excellent photovoltaic performances, have serious drawbacks hampering large-scale production and application.

In contrast to halide perovskites, which have been the subject of many experimental and theoretical investigations, the physico-chemical characterization of chalcogenide perovskites is seriously scarce and the thermodynamic properties are not available, most of the recent literature consisting of computational works aimed at predicting phase stability and structural and optoelectronic properties. The scarcity of experimental information is partly due to the challenges posed by the synthesis of these materials, requiring harsh conditions, for example very high temperatures; in this regard, a milder procedure has recently been developed by our group for the preparation of $BaZrS_3$, $BaHfS_3$, and their solid solutions [2]. Moreover, also the production of thin films of chalcogenide perovskite materials remains a challenge. Conversely, the decomposition behavior at high temperature is apparently unexplored in the literature.

In order to give a contribution in filling this gap, the present work is focused on the vaporization behavior of the $BaZrS_3$ sulfide perovskite and its BaS precursor and on the experimental determination of the associated thermodynamic properties. By using the Knudsen effusion mass spectrometry technique, it was possible to study the gas-releasing decomposition processes of the perovskite in a wide temperature range. The BaS and Ba_2S_2 molecules were identified in the vapors produced at high temperature and subjected to thermodynamic analysis with the help of Coupled-Cluster *ab initio* calculations.

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THERMODYNAMIC STUDY OF SnI_4 SUBLIMATION IN A LOW TEMPERATURE RANGE (313 K – 340 K) BY EFFUSION TECHNIQUES

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The interest raised by tin halide hybrid perovskites as potential alternative to Pb-based ones in photovoltaic applications, motivated by concerns for health and environment associated to the presence of lead, prompts a thorough study of their stability in conditions easily attainable during operations. Notwithstanding the current scarcity of information about tin perovskites decomposition, their main disadvantage is known to be represented by the easy oxidation of tin divalent state (the only one that should in principle be present in perovskites) to the tetravalent one, with the formation of decomposition products containing Sn^{4+}. In particular, the formation of SnI_4 upon photo- or thermal degradation has been already observed [1] and, since this compound is more volatile than SnI_2, it could be released as a gaseous decomposition product from solar cells at temperatures attainable during operations. For this reason, it is very important to have well-assessed vapor pressure values for SnI_4, in particular in the temperature range of interest for photovoltaic devices. However, although some vapor pressure measurements were performed in the past [2], none of the earlier studies examined temperatures below 350 K, and all the reported experiments were carried out using static methods.

Herein, the first investigation of the sublimation behavior of tin tetraiodide, SnI_4, using effusion-based techniques, is described. The temperature range covered in these experiments (313 K – 340 K) was lower than in previous studies. Knudsen Effusion Mass Loss (KEML) measurements were performed using effusion cells with different orifice sizes, in the range (317.1 – 339.6) K. Vapor pressures, which were found to be independent of the orifice size, were measured in the range (0.13 – 1.10) Pa. By the Clarke and Glew fit of experimental data, standard molar enthalpy and Gibbs energy of sublimation at 298.15 K of $(88.1 \pm 0.9)\ kJ\cdot mol^{-1}$ and $(39.0 \pm 0.1)\ kJ\cdot mol^{-1}$, respectively, were obtained. Knudsen Effusion Mass Spectrometry (KEMS) experiments were also performed, in the range (313.3 – 331.7) K, and the sublimation enthalpy from these measurements resulted to be in good agreement with the KEML value, although the measured vapor pressures were significantly higher. All the vapor pressure data were also analyzed by the third-law method. Additionally, results of DFT and *ab initio* calculations, performed to estimate the molecular properties of $SnI_4(g)$ and the extent of the gas-phase dissociation to SnI_2 and I_2, are reported. Experimental results are compared with the literature data available for both sublimation and evaporation properties of SnI_4.

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CRYSTALLIZATION KINETICS OF CROSS-LINKED POLYMERS

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The presence of covalent cross-links between the polymer chains causes increased mechanical strength and chemical stability, as well as the shape memory effect. Despite the widespread use of cross-linked polymers and the appearance of new applications, there is currently no complete understanding of the effect of cross-link density on the crystallization and nucleation kinetics under various conditions. The experimental data on crystallization at high supercooling are difficult to obtain since the conventional DSC method is limited by the scanning rates (up to 500 K/min) and timescales (seconds and longer).

Such limitations can be overcome with the fast scanning calorimetry (FSC) method. FSC allows to achieve scanning rates up to 1 MK/s and time constants as low as 1 ms by minimizing the cell size and operating with nanogram-scale samples. Previously, we have reported that an increase in the cross-link density leads to a monotonic decrease in the critical crystallization cooling rate, overall crystallization and nucleation rates at constant temperature of the cross-linked polycaprolactone (PCL) [1] and poly(butylene terephthalate) (PBT) [2].

Recently, we studied the crystallization kinetics of polyamide 12 (PA-12) samples irradiated with a high-energy electron beam. A series of samples with an absorbed dose from 0 to 600 kGy was obtained. The gel fraction and FTIR spectra were analyzed in order to characterize the irradiated samples. The gel fraction is present in the samples irradiated with at least 50 kGy and grows up with increasing dose. The critical cooling rate and the overall crystallization rate at constant temperature of the cross-linked PA-12 samples were determined by FSC. These rates also decrease monotonously with an increase in the dose absorbed by the samples leading to a higher degree of cross-linking. This trend can be explained by the growth of the diffusion activation energy and the work of formation of a critical crystal nuclei linked to an increase in the viscosity of the system. The obtained results provide an additional evidence for a general relationship between the crystallization kinetics and the cross-link density for the polymers differing by the chemical nature and cross-linking method.

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PHASE EQUILIBRIA, SALTING-IN–SALTING-OUT EFFECTS AND EXTRACTIVE CRYSTALLIZATION IN THE TERNARY POTASSIUM IODIDE–WATER–DIISOPROPYLAMINE SYSTEM IN THE RANGE 0-60 °C

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Low molecular weight amines are used as antisolvents in the process of extractive crystallization of salts from their aqueous solutions. This process is environmentally cleaner and economically more favorable than the traditional method of solution evaporation. Our research is devoted to polythermal study of phase equilibria in mixtures of components of the ternary potassium iodide – water – diisopropylamine system in order to find out the possibility of amine extraction from aqueous solutions under the action of potassium iodide and extractive crystallization of this salt.

Phase equilibria in mixtures of components were studied by the visual-polythermal method along fourteen sections of the composition triangle of the ternary potassium iodide–water–diisopropylamine system in the range from 0.0 to 60.0 °C. The introduction of potassium iodide into the mixture of the critical composition of the water–diisopropylamine binary system leads first to an increase of the critical temperature and then to its sharp decrease up to the temperature of the critical tie line formation (4.8 °C). Obviously, with increasing temperature and salt concentration there is a loss of salting-in properties of potassium iodide and a transition to salting-out.

In the studied system in the interval 0.0-4.8°C, the phase diagram is characterized by the presence of a solubility line separating the fields of homogeneous and saturated solutions. On the isotherm at 4.8 °C the critical tie line of the monotectic state appears on the field of saturated solutions. As the temperature increases, the critical node transforms into a monotectic triangle with adjacent fields of saturated solutions and delamination. Such a set of phase states, characteristic of isotherms of ternary systems with mixtures of binary homogeneous system salting-out, is realized in the interval 4.8-27.3 °C. A critical point appears on the isotherm at 27.3 °C on the side of the triangle corresponding to the critical composition of the liquid system. In the interval 27.3-37.6 °C there are two isolated delamination fields with critical points on the isotherms, which confirms the salting-in effect of small salt concentrations on heterogeneous liquid mixtures. Significant concentrations of salt have a salting-out effect on water–amine solutions due to the destruction of their structure. As the temperature increases, the salting-in effect of salt weakens, and on the isotherm at 37.6°C, the delamination fields touch critical points. At higher temperatures, there is a single delamination field on the isotherms.

To evaluate the efficiency of salting-out diisopropylamine, we determined the dependence of its distribution coefficient K_d between equilibrium liquid phases of the monotectic on temperature. Above 35.0 °C, the organic phase is significantly enriched in amine, while in the aqueous phase its content is insignificant. High values (more than 200) of the K_d of diisopropylamine in the range of 35.0-60.0 °C indicate the effectiveness of potassium iodide as an amine salting-out agent.

The dependence of the yield of potassium iodide crystals on temperature and amine concentration was revealed. It was found that the maximum yield of salt (58.6%) was found at 35.0 °C and introduction of 90 wt.% diisopropylamine. These conditions can be considered as optimal, since their change leads to a significant decrease in the salt yield. The content of diisopropylamine in the organic phase of the monotectic state at 35.0°C is favorable for its regeneration.

PHYSICO-CHEMICAL SUBSTANTIATION OF THE METHOD OF EXTRACTIVE CRYSTALLIZATION OF SALTS BASED ON THE ANALYSIS OF PHASE DIAGRAMS OF TERNARY SALT – WATER – ANTISOLVENT SYSTEMS

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The advantage of obtaining salts by the method of extractive crystallization is its lower energy consumption compared to traditional solution evaporation and the possibility of extracting salts that have a low temperature coefficient of solubility or decompose during solution evaporation. The purpose of the work was to develop a physicochemical substantiation of the method of extractive crystallization of salts from aqueous solutions with the possibility of choosing the optimal conditions for the process based on the study and analysis of phase diagrams of ternary salt – water – amine systems. Phase equilibria and critical phenomena in a number of ternary systems were studied and isotherms of phase states at different temperatures were constructed. In all systems the compositions of equilibrium phases of the monotectic state were determined, which made it possible to calculate the salt yield depending on the crystallization conditions. It was found that the determination of optimal conditions for the process is possible on the basis of analyzing the phase diagrams of the systems in a certain temperature range. However, this way is labor-intensive and time-consuming. The revealed regularities of extractive crystallization allowed us to significantly reduce the amount of experimental work to identify the best conditions for salt extraction and to propose the following algorithm.

1. The choice of a suitable antisolvent is determined by a number of conditions, mainly its physicochemical properties. For most salts, the use of aliphatic amines is optimal.
2. Selection of the optimum temperature range for phase diagram studies. It was found that the interval of 10-40ºC is optimal for all studied systems. It is convenient for technological processes, since it does not require significant energy costs for maintaining high or low temperatures.
3. Study of phase equilibria. The minimum number of sections of two types with optimal position on the concentration triangle is selected for the subsequent polythermal study of mixtures of components.
4. Phase diagram analysis. On the basis of polythermal data, the monotectic state triangle is plotted on the isotherms of the ternary system at several temperatures and the compositions of the equilibrium liquid phases of the monotectic state are determined graphically.
5. Determination of optimal conditions of salt extraction from aqueous solutions. With the help of Mathcad working document developed by us, calculations are carried out and dependences of salt yield on antisolvent concentration and temperature are revealed with visualization and analysis of the results.
6. Determination of optimal conditions of extractive crystallization. Select the temperature, which combines a high yield of salt crystals with an acceptable content of antisolvent in the organic phase of the monotectic state for its effective regeneration.

The proposed algorithm is tested on two ternary systems. The calculation results obtained on the basis of a limited set of data and analysis of complete phase diagrams of the systems are in good agreement. The developed algorithm makes it possible to reduce the labor-intensive experiment, material and time costs by about 6-8 times, i.e., to carry out an express evaluation of the effectiveness of this antisolvent for the extractive crystallization of a particular salt without selecting phases and their chemical analysis.

STUDY OF THE CONDITIONS FOR THE SYNTHESIS OF GLASS-CERAMICS FROM ULTRADISPERSE PRECURSORS BASED ON Bi_2O_3-B_2O_3-BaO GLASS AND YAG BY THERMAL ANALYSIS METHOD

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In this work, the thermal conditions for the formation of a new glass-crystalline material of optical quality with nano-sized crystals $(Y_{1-x}R_x)_3Al_5O_{12}$ (R – Er, Nd, Sm, etc.) are investigated.

The development and use of an original method for converting molecular dispersions of precursors into a compacted charge - a source for obtaining a new glass crystal with a nanocrystalline R:YAG phase - is a current direction that ensures the development of technology for producing materials for photonics. The practically unlimited variability of the composition of the charge, which combines the properties of glass and crystal, provides a convenient method for the manufacture of optical devices using additive technology, including selective laser sintering.

Physico-chemical characterization of the processes for obtaining a new multifunctional glass-crystalline material with a crystalline base $(Y_{1-x}R_x)_3Al_5O_{12}$, where R = {Er, Nd, Sm, etc.}, together with technological solutions for the synthesis of an ultradisperse precursor in the form of a glass-forming charge and subsequent laser formation of glass-crystalline materials planar photonics devices is a complex and scientifically fundamental problem.

The work presents:

-Development of new methods for the synthesis of glass crystal precursors with an expanded macro composition $[(R_2O_3)_x(Y_2O_3)_{1-x} – Al_2O_3] – [Bi_2O_3 – B_2O_3 – BaO]$.

-Results of thermoanalytical determination of the temperature-time conditions for the formation of glass crystals from the charge using data on the kinetics of phase and chemical transformations, processed using original methods based on an extended version of the Kolmogorov-Mahle-Johnson theory of crystallization.

-Kinetic patterns of the formation of the crystalline phase, which, with thermodynamically allowed factors, specify the temperature-time regimes of the formation of borate glass crystal from the prepared charge.

-Research on the possibilities of an additive laser method for the formation of glass-crystalline photonic elements that are transparent in the visible and IR regions of the spectrum.

The results of the work form a scientific and technological basis in the materials science of photonic materials for the implementation of additive production of optical chips in the near-IR and visible regions of the spectrum.

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PATTERNS OF INTERACTION BETWEEN PEPTIDES OF VARIOUS STRUCTURES AND PYRIMIDINE NUCLEIC BASES IN A BUFFERED SALINE MEDIUM ACCORDING TO THE THERMODYNAMIC PARAMETERS OF THE PROCESS

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The interactions of oligopeptides and proteins with nucleic acid bases as RNA fragments underlie many biochemical processes, including protein replication, virus introduction, and genetic engineering. In an aqueous medium, the formation of complexes between them is the result of the interaction of hydrated particles, and this significantly affects the binding patterns and stability of the complexes. In this work a set of thermodynamic parameters for the complexation of peptides of various structures with pyrimidine nucleic bases (uracil, thymine, cytosine) in a phosphate buffered saline medium have been obtained. From the analysis of the data, several important patterns of binding of peptides to pyrimidine nucleobases have been revealed.

Complexes of uracil exhibit a greater stability compared to cytosine complexes. The introduction of a methyl substituent to the C5 atom in the heterocycle at going from uracil to thymine increases the ability to bind peptides.

No regularity depending on the charge of the peptide is observed in the values of $\lg K_r$, $\Delta_r G$, $\Delta_r H$, $T\Delta_r S$ for binding to pyrimidine nucleobases.

The effect of the structure of the peptide and the nucleobase on the thermodynamic parameters of complexation is manifested in the fine balance of the enthalpy and entropy factors of the process. The formation of complexes with uracil is controlled by the dominant entropy factor $T\Delta_r S > -\Delta_r H$. In the formation of complexes with cytosine, as a rule, the enthalpy factor dominates $-\Delta_r H > T\Delta_r S$.

Negative values of the Gibbs energy of complexation tend to decrease with an increase in the number of potential H-binding sites of a peptide from 5 to 10. The decrease in negative $\Delta_r G$ values may be associated with an increase in the number of formed H-bonds of the peptide with the nucleic base, which leads to a loss in the entropy factor.

It was found that positive values of entropy change during complex formation increase with increasing hydrophobicity index of the peptide $\mathrm{Log}P'$. The relationship between peptide hydrophobicity and the entropy factor of complexation can be interpreted within the framework of the overlapping hydration sphere model. When the hydration shells of the hydrophobic peptide and the nucleic base in the complex overlap, most of the water molecules are displaced into the bulk of the solvent. It leads to a more favorable entropy factor. Strengthening the hydrophobic properties of the nucleic base from uracil to thymine due to the additional CH_3 group also causes an increase in the favorable entropy factor in the complexation with peptides and in the stability of complexes.

The effect of stabilization of the solvent structure in the environment of uracil molecules was shown based on volumetric properties (standard molar volume, transfer volume, first and second derivatives of molar volume with respect to temperature). The stabilization effect is enhanced by the addition of peptides. This is a consequence of blocking the polar groups of uracil due to their hydrogen bonding with the amino and carboxylate group of the peptide.

The formation of hydrogen bonds between peptides and pyrimidine bases was proven by quantum chemical modeling. In the complexes, peptides act as polydentate ligands. Sites of the hydrogen bonding are charged NH_3^+ and COO^- groups at the ends of the main and side chains of the peptide as well as polar amide fragments in the middle of the chain. Possible optimized structures of the complexes are being considered.

THERMOCHEMISTRY IN 21ST CENTURY – QUO VADIS? IN SILICO ASSISTED DIAGNOSTICS OF AVAILABLE THERMOCHEMICAL DATA

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Which comes first, experiment or theory? The answer is obvious – the experiment comes first. But how to be sure that the result of the experiment is reliable? Perhaps the crucial criterion is that the result should be consistent with the network of knowledge already available. In this study, we propose a step-by-step algorithm for quality diagnostics of thermochemical data on enthalpies of formation and enthalpies of phase transitions of organic compounds. The consistency of the data is studied and established using empirical structure-property correlations, as well as using high-level quantum chemical calculations. The diagnostic algorithm is exemplarily demonstrated on a series of organic compounds for which conflicting thermochemical data were available.

DYNAMIC CALORIMETRY AS A RESULT OF THEORETICAL PROCESSING OF THERMAL ANALYSIS DATA USING THE EXAMPLE OF SYNTHESIS OF BORATE GLASS-CERAMICS

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Modern and highly stable thermal analysis instruments are increasingly used to determine the thermodynamic and kinetic characteristics of materials synthesis processes and their properties.

In "DSC heat flow" devices, it is accepted [Borchard, 1957] that the $\boldsymbol{S}_{\text{DSC}}$ signal is proportional to the specific heat flow:

$$\boldsymbol{S}_{\text{DSC}} = \underline{C}(T)\frac{d(H/m_0)}{dt} = \underline{C}\left(\dot{T}\boldsymbol{c_P} + Q_M\dot{\boldsymbol{\alpha}}\right), \qquad (1)$$

where $\dot{T}$ is the heating rate of the sample, $\underline{C}(T)$ is the instrument calibration function, $\boldsymbol{c_P}$ is the specific heat (per unit mass of the sample) of the thermally analyzed substance in a mode free from interphase transitions in temperature interval, $Q_M = \Delta_{tr}H/M$ is specific heat transitions between states, $\Delta_{tr}H$ – enthalpy of transition.

Differential shape of AKM, determining the rate of crystallization

$$\dot{\alpha} = k\, n\, \alpha^{1-1/n}\left(1 - \alpha^{1/p}\right)^{1+p/n}, \qquad (2)$$

Integral form of the AKM, which determines the degree of transformation

$$\alpha(t, T) = \frac{1}{(1+1/\tau^{n/p})^p}\ .\ (\tau = k{\cdot}t) \qquad (3)$$

The applied kinetic model (AKM) (2, 3) combines the Kolmogorov-Johnson-Mahle (KJM) theory of crystallization and the semi-empirical Erofeev model with parameters E_a and A, as part of the Arrhenius rate constant k; n is the dimensional parameter of the (KJM) theory and the diffusion parameter p.

$$\dot{\alpha} = \bar{k}n\alpha^{1\text{-}1/n}\left(1 - \alpha^{1/p}\right)^{1+p/n}. \qquad (2')$$

$$\bar{k} = k\left(1+\frac{(1 - T_0/T)E_a}{RT}\right), \qquad (3')$$

The addition of the applied KJM theory with the thermodynamic factor $F = \frac{1}{\left(1+\left(\frac{T_{tr}-T_0}{T-T_0}\right)^{h\,\Delta_{tr}\tilde{S}}\right)}$ at $\alpha(t,T) = \frac{1}{(1+1/\underline{\tau}^{n/p})^p}$, $\underline{\tau} = \underline{\kappa}t$, $\dot{\alpha} = \overline{\underline{\kappa}}n\alpha^{1-1/n}(1-\alpha^{1/p})^{1+p/n}$, $\overline{\underline{\kappa}} = \kappa F\left[1 + h\frac{\Delta_{tr}H}{RT_{tr}}(1-F)\right]$, which is necessary to describe the phase transition (PT), leads to the replacement of its Arrhenius kinetics with diffusion-controlled ones, corresponding to the physical theory of phase transitions. This PT model can be used for phase-chemical transformations during the production of materials. The PT model was tested on the problem of determining the dependence of the temperature and enthalpy of fusion on the atomic mass of Ge isotopes.

To process thermoanalytical data on the heat capacity of crystalline, liquid and glassy states, including the glass transition region, a quasiparticle (vacancy) theory was used, which determines the full set of standard thermodynamic functions of these states of aggregation. Processing the experiment is reduced to finding the parameters of the overall mathematical model using the least squares method.

The material of the report will be illustrated by the results of studies of borate glasses Bi_2O_3-BaO-B_2O_3:RB doped with Sm (Nd) borates for multifunctional photonics devices.

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SALTING-OUT OF POLYETHYLENE GLYCOL-1500 (PEG-1500) FROM AQUEOUS SOLUTIONS BY CESIUM CHLORIDE AND NITRATE IN THE RANGE OF 10-100°C

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Cesium belongs to rare alkali metals and its compounds have a wide range of applications. The demand for cesium salts in industry and technologies considerably exceeds their production. For extraction of cesium salts from natural chloride brines and technological nitrate solutions polyethylene glycols are proposed to be used, which determines the relevance of the study of solubility in ternary cesium salt – water – polyethylene glycols systems.

Our study is aimed at revealing the influence of cesium chloride and cesium nitrate on the phase behavior of the binary system water–PEG-1500 by phase diagram analysis, evaluating the effect of PEG-1500 salting by cesium salts, and investigating the solubility of salts in binary liquid mixtures. Phase equilibria in mixtures of components were studied by the visual-polythermal method by cross sections of different types of composition triangle of two ternary cesium chloride (nitrate) – water – PEG-1500 systems in the range of 10-100°C. It is found that the following phase states are realized in the mixtures of components: saturated and homogeneous solutions, monotectics, eutonics, and delamination. The temperature dependence of the critical solution composition for the investigated ternary systems was found. Polythermal data allowed to reveal topological transformation of phase diagrams of both systems with temperature change. In the system with cesium chloride below 13.7°C and in the system with cesium nitrate below 78.8°C, a smooth line of salt solubility in mixtures of water and PEG-1500 exists on the isotherms. At 13.7°C for cesium chloride and 78.8°C for the system with cesium nitrate, a critical point appears on the solubility line and a critical monotectic tie line appears on the field of saturated solutions. As the temperature increases, the tie line transforms into a monotectic triangle with adjacent fields of saturated solutions and delamination. Further increase of temperature leads to enlargement of the area of monotectic triangle due to rise of solubility of salts and strengthening of their salting-out action. On a number of isotherms of the studied ternary systems there is also a triangle of the eutonic state (equilibrium of the liquid phase with crystals of salt and PEG-1500).

To evaluate the effect of salting-out PEG under the influence of salts, the distribution coefficient of PEG-1500 between the phases of monotectics at different temperatures was calculated. It was found that with increasing temperature it increases more significantly in the system with cesium chloride (takes values > 900) than with cesium nitrate. This indicates a stronger salting-out effect of cesium chloride compared to cesium nitrate. Cesium chloride has significantly higher solubility over the entire temperature range of the study. The topological transformation of phase diagrams of the studied systems with temperature change has some differences.

Thus, the possibility of using the visual-polythermal method to study phase states in systems containing PEG-1500 in a wide temperature range was confirmed for the first time. For the first time for ternary systems salt – water – PEG-1500 the temperatures of the onset of delamination were established. The system with cesium chloride was proposed to be used as an extraction system at relatively low temperatures. Significant decrease of solubility of salts in water at introduction of PEG-1500 promotes the process of extractive crystallization of cesium chloride and nitrate, their purification and separation from aqueous solutions.

CONTACT MELTING IN METAL NANOSYSTEMS: MOLECULAR DYNAMICS SIMULATION

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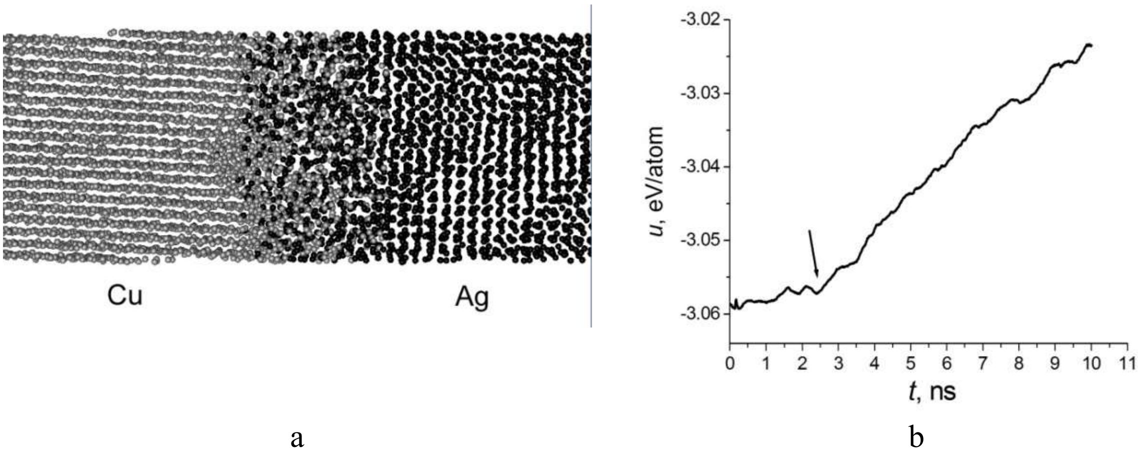
To memory of Prof. V.A. Sozaev
(1949 - 2021)

Contact melting (CM) is directly related to technologies of soldering, sintering, metallization of ceramics and semiconductors. At the same time, as noted in [1], even CM in macrosystems has clearly not been studied enough. This opinion may be referred to an even greater extent to nanosystems, including bimetallic ones. CM is most typical for eutectic systems, for example, for the Ag-Cu bimetallic pair. Paper [2] is devoted to molecular dynamics (MD) modeling of CM in the bulk Ag-Cu system. Initially, in our MD experiments, we planned to study CM induced by the contact between Ag and Cu nanoparticles of spherical and cubic shapes. However, during the research in this direction, it became clear that in a bimetallic system of two monometallic particles, CM is complicated by other parallel phenomena, including sintering, surface diffusion and segregation of components. Taking this into account, a more detailed MD study of the laws and mechanisms of CM was carried out using the pattern of a flat bimetallic layer, nanosized in thickness. Figure 1a shows a configuration of an Ag-Cu bilayer, demonstrating both interdiffusion of components and CM. Melting in the contact zone leads to some jumps and changes in the slope of the kinetic dependence $u(t)$ of the specific (per atom) cohesive energy u (Figure 1b) in the course of annealing the system under consideration.



a b

Figure 1. CM in the Ag-Cu bimetallic layer. Panel (a) presents a snapshot corresponding to a result of annealing at temperature T = 1060 K for time t = 5 ns; panel (b) demonstrates the $u(t)$ dependence. The arrow in Fig. 1b indicates the appearance of the liquid phase.

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DATABASES FOR ALLOYS WITH REFRACTORY ELEMENTS: PROBLEMS OF STABLE AND METASTABLE EQUILIBRIA

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Refractory elements are widely used as alloying additions in the wide range of high-temperature materials such as steels and superalloys. Even small additions of these elements have an essential influence on mechanical and exploitation properties of the alloys, especially strength at room and elevated temperatures, fatigue resistance etc. One of the most obvious examples is formation of nanosized particles of Nb, V and Ti carbides and nitrides in steels.

Special interest to these elements appeared with development of high-temperature complex concentrated alloys, which is connected with increase of the working temperatures of High temperature CCA above existing nickel superalloys (above 1100C).

The constancy of the phase composition is one of the key requirements for materials working at elevated temperatures, since the uncontrolled process of phase formation during long-term operation is accompanied by changes in the microstructure and, as a consequence, leads to a sharp decrease in the operational properties (mechanical, corrosion, etc.) of the structural materials. In order to predict the possibility of such processes and the consequences of their occurrence for a specific material of a given composition, it is necessary to study in detail the phase relationships in the systems of interest in a wide range of temperatures and compositions under conditions as close as possible to equilibrium. Experimental study of phase diagrams of systems with more than two components requires significant time and material resources. Therefore, one of the global trends in this field of science is the combination of experimental and theoretical calculations using the apparatus of modern chemical thermodynamics.

The purpose of this presentation is to give an overview of existing thermodynamic databases, phase diagrams and present status of works carried out on the development of databases with refractory elements. We will highlight some of the issues the assessor faces during critical evaluation of experimental and theoretical data using some recent examples.

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THIRD-GENERATION CALPHAD ASSESSMENT OF SIO2-GEO2 AND SI-GE SYSTEMS AT ATMOSPHERIC PRESSURE

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Compounds of quasi-binary SiO_2-GeO_2 systems and binary Si-Ge systems have a wide range of applications, including the creation of new glass materials, piezoelectric materials, etc. The binary Si-Ge system has been evaluated twice, but the data for it is unreliable below room temperature. For the quasi-binary system SiO_2-GeO_2, the available versions of this system contain errors and do not coincide with the data for pure SiO_2 and GeO_2. Therefore, the aim of this study was to reassess the corresponding systems using the latest available experimental data and 3rd generation CALPHAD models [1,2].

The extended Einstein model [1] is intended to provide a more physically based description of solid-crystalline phases from zero K to temperatures significantly above the melting point. The liquid two-state model [2] can be used to describe the liquid phase both inside and outside its stability regions. The two-state liquid model makes it possible to describe the decrease in the heat capacity of a liquid with increasing temperature, which is assumed by experimental data. The description of pure elements and compounds using 3rd generation CALPHAD models was previously carried out in [3,4,5]. The proposed models make it possible to describe reliably the thermodynamic properties of both stable crystalline and liquid phases in the temperature range from zero K to temperatures significantly above the melting point.

The thermodynamic description of the Si-Ge system has been improved through the introduction of new models of pure elements, as a result a more accurate description of the liquid phase above the melting point was obtained. Also, for the first time, the evaluated Si-Ge database allows us to make reliable predictions of the heat capacity of pure silicon and germanium in the amorphous state at low temperatures. The phase diagram of the SiO_2-GeO_2 system evaluated in this work allows more accurate predictions of the solubility of components in α- and β-quartz and provides reliable predictions of phase relationships below room temperature. Modeling for SiO_2 based on analysis of the latest literature data allowed us to exclude tridymite from the list of stable phases. Although restabilization of tridymite in the quasi-binary SiO_2-GeO_2 system has not been reported, it was not included in the current assessment, unlike previous versions of the phase diagram.

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The authors gratefully acknowledge the financial support of the Program “Chemical Thermodynamics and Theoretical Material Science” (№ 121031300039-1), Lomonosov MSU.

FLUID WORKBENCH: SOFTWARE TOOL FOR CALCULATION OF THERMO-PHYSICAL AND OPTIC PROPERTIES OF GASES AND PLASMA. APPLICATION FOR ACCURATE CALCULATION OF TRANSPORT AND RADIATION PROPERTIES OF LOW-TEMPERATURE PLASMA OF NOBLE GASES

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Fluid Workbench program suite consists of three parts: the database of substances characteristics, calculating modules, and graphical interface. The database contains information that is required in calculating transport and radiative properties of mixtures. Properties of more than 5000 individual atoms and molecules are stored in the database including NASA7, NASA9, or IVTAN coefficients for calculating thermodynamic properties, electronic levels structure of substances, and pair interaction potentials or collision integrals.

This work presents the methodology and detailed set of data for transport and radiation properties of noble gases (He, Ne, Ar, Kr, Xe) and their mixtures in wide range of temperatures (T=300-50000 K) and pressures (P=0.1-300 bar). This knowledge is necessary for predictive modelling of complex chemically and optically active systems.

Transport coefficients were calculated in the assumption of the local thermal and chemical equilibrium (LTE) in the framework of Chapman-Enskog theory by using the Fluid Workbench program suit. All coefficients were calculated in the second approximation by the accurate formulas of Chapman-Enskog theory. Effective thermal conductivity was calculated as a sum of translational thermal conductivity and reactive one, which was obtained from the advanced version of Butler-Brokaw formula.

Absorption coefficients of noble gases plasma were calculated in LTE assumption based on data set of electronic energy levels, transition probabilities of atoms, potential energy curves (PEC) and transition dipole moments of excimers. The generalized approach for bound-bound transitions together with Kramers-Unsold-Biberman model for photoionization were used for atoms. Photoionization cross section has correction of the behavior near threshold in accordance with model of quasistatic plasma microfield. The characteristics of probabilities for unknown or not well-defined transitions between high excited states were calculated by method of quantum defect using quasiclassical approach for wave functions. Born-Oppennheimer, Frank-Condon approximations and Honl-London factor were used for calculation of electronic-vibrational-rotational absorption spectrum of excimers. PEC and transition dipole moments of some excimers were calculated by Quantum Chemical methods. Doppler, quasistatic, impact, Stark, van der Vaals broadening mechanisms were taken into account for line shape.

Presented results of calculation of transport coefficients cover a very wide range of conditions (temperatures and pressures). For high temperatures the ion-neutral interactions were taken into account. For calculating collision integrals, the most recent theoretical and experimental data on the scattering cross-sections and interaction potentials was used.

PHASE EQUILIBRIA OF ALLOYS BASED ON THE CR-TA-W-V SYSTEM

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Complex concentrated alloys (CCA), consisting of five or more basic elements, have more attractive mechanical and structural properties compared to conventional alloys. The most heat-resistant group of CCAs consists of refractory elements with a bcc lattice, such as Hf, Ti, W, Ta, Mo, etc. CCAs of this type are called refractory complex concentrated alloys (CCAs). For oxidation resistance and reduced density, these materials are also doped with Cr and V elements, which tend to form Laves phases with refractory elements. It is believed that the appearance of these phases deteriorates the mechanical properties of these alloys.

Currently, there is a serious lack of publications containing experimental studies of phase equilibria in these systems, therefore, in this work, experimental phase equilibria in the Cr-Ta-W-V system and its subsystems were studied. The alloys were subjected to arc melting and homogenization at 1500, 1400 and 1100 °C for various times up to 500 hours. The resulting microstructures were characterized using scanning electron microscopy (with EPMA) and X-ray diffraction. Isothermal sections of the Ta-W-V, Cr-Ta-W and Cr-Ta-V systems were obtained.

Based on the data obtained, the solubility ranges of solid solution phases were refined. New phase diagram features have also been identified, such as miscibility gaps and new intermetallic phases.

The authors gratefully acknowledge the financial support of the Program "Chemical Thermodynamics and Theoretical Material Science" (№ 121031300039-1), Lomonosov MSU.

SELF-ASSEMBLY AND BIOLOGICAL ACTIVITY OF HOMOLOGOUS SERIES OF PYRROLIDINIUM AMPHIPHILES

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The application scope of surfactants is quite wide: from detergents to drug delivery. One of the greatest scientific interests are cationic amphiphiles with heterocycle-based headgroups, which are capable of diverse range of interactions with biological membranes. In this study new series of cationic surfactants based on pyrrolidine functionalized by a hydroxyethyl fragment (MPS-n(OH), where n=10, 12, 14, 16; Figure 1) were synthesized. The aim of this study is to identify patterns of self-assembly and assess the functional properties of synthesized amphiphiles.

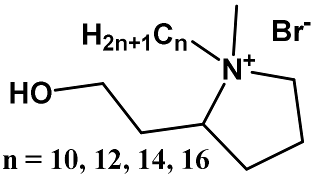

Figure 1. Structural formulas of surfactants studied.

The critical micelle concentrations (CMC) of MPS-n(OH) were determined using tensiometry, conductometry, spectrophotometry, and fluorimetry. The amphiphilic molecules reduce the surface tension at the water-air interface to 40 mN/m. The CMC of the MPS-10(OH) decreases 15 times compared with the hexadecyl derivative (from 15 mM to 1 mM). The reliability of the data is demonstrated by the good agreement between the results of the different methods used. Thermodynamic parameters of adsorption and micellization were calculated based on surface tension isotherms. An increase in the alkyl chain length gradually reduces the maximum surface excess value, and the processes of micellization and adsorption become more favorable, which is supported by more negative values of Gibbs free energy. The solubilizing capacity of pyrrolidinium surfactants was investigated toward hydrophobic dye Orange OT and non-steroidal anti-inflammatory drugs indomethacin and naproxen. It was found that the hexadecyl homologue has the highest solubilizing capacity toward all solutes. To assess the biological activity of the MPS-n(OH), i.e., hemolytic, antibacterial, antifungal, and cytotoxic activities, were investigated. It was shown that the MPS-10(OH) and MPS-12(OH) demonstrate a low level of hemolysis (HC_{50} ≥200 μM), while MPS-14(OH) and MPS-16(OH) have high biological activity against methicillin-resistant strains of *Staphylococcus aureus* MRSA-1 and MRSA-2 (minimum inhibitory concentration =0.5 μg/mL).

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EXPERIMENTAL STUDY ON THE PHASE EQUILIBRIA OF THE PB-SM SYSTEM

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Investigation of the phase equilibria in the Pb-Sm system is crucial for a wide range of applications, including creation of materials with special magnetic properties and for electronic devices. A comprehension of the thermodynamic properties and phase behavior of Pb-Sm alloys is also indispensable for the design, optimization, and safe operation of nuclear reactors.

The tentative phase diagram of the Pb-Sm system was published by Savitsky [1]. In the Pb-Sm system, the existence of the compound SmPb3 is known, but the data on its melting temperature presented in the literature are inconsistent. According to [1] the SmPb3 phase melts congruently at a temperature of around 1040°C, however, in a study by Palenzona [2], the melting temperature of SmPb3 according to dynamic differential calorimetry data was reported to be 970°C. In the literature, there are also data on the solubility of samarium in liquid lead: in study [3], these data were obtained during the study of the alloy using the electromotive force method, and in work [4] using the isothermal dissolution method. However, the discrepancy in the values of samarium solubility exceeds the experimental error stated in the studies.

The purpose of this work is to clarify the phase diagram of lead – samarium system in a lead-rich area.

For the identification of phase equilibria during crystallization there were prepared a set of samples by arcmelting in argon atmosphere. Alloys were studied by scanning electron microscope / electron probe micro-analyzer (SEM/EPMA), differential scanning calorimetry (DTA), and X-Ray diffraction (XRD) analysis.

The phase equilibria of the Pb-Sm system were experimentally studied in the concentration range of Sm from 0 to 25 at. %. Additionally, the temperature and composition of the eutectic between pure lead and the SmPb3 compound were refined in the study.

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FORMATION THERMODYNAMICS OF CARBAMAZEPINE COCRYSTALS

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Pharmaceutical cocrystals have aroused considerable interest in the scientific community as a potential approach to fine-tune the biopharmaceutical and physicochemical properties of active pharmaceutical ingredients. Despite the increasing popularity of cocrystallization and the proliferation of publications reporting new cocrystals, the thermodynamic aspects of cocrystals in relation to the coformer nature, which are crucial for understanding the formation, driving force and stability, remain relatively unexplored.

In the present work, the thermodynamics of formation of the twelve carbamazepine cocrystals were explored in depth by the cocrystal solubility method. Carbamazepine (CBZ) is an anticonvulsant drug that has been widely used in clinics for more than 50 years to treat epilepsy, trigeminal neuralgia and bipolar disorder [1]. As a result, the thermodynamic parameters of the CBZ cocrystal formation with benzamide, 4-hydroxybenzamide, isonicotinamide, salicylic acid, cinnamic acid, 2,4-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3-acetamidobenzoic acid, 4-acetamidobenzoic acid, methylparaben, aspirin and indomethacin were evaluated. In each case, the negative value of the Gibbs free energy indicated that cocrystallization is a thermodynamically favored process driven by enthalpy or entropy. The relation between the cocrystal molecular packing features and the thermodynamic parameters was observed. The entropically favored cocrystals of carbamazepine exhibit stacking of the isolated structural motifs (dimers, rings, or chains) via weak noncovalent interactions. In contrast, the cocrystals with enthalpy-determined formation processes are characterized by the formation of strong hydrogen bonds between the main structural motifs.

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This work was supported by the Russian Science Foundation (№ 22-13-00031).

INVESTIGATION OF STANDART CALORIMETRIC AND VOLUMETRIC PROPERTIES OF GLASSES $(Ge_{0.21}Te_{0.79})_{1-x}(AgI)_x$ (x = 0.1 – 0.5) WITH A VARYING CONTENT OF SILVER IODIDE

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Chalcogenide glasses based on germanium tellurides are promising materials for infrared optics due to their high transparency in the mid-IR range (3-25 microns) and high chemical resistance. Those glasses find application as fiber-optic light guides, sensors for the analysis of liquid and gaseous media in IR spectroscopy, and in electrical engineering for the manufacture of chip components.

Information on thermodynamic properties and thermophysical characteristics within the established boundaries of a particular physical state is necessary to determine the conditions for the synthesis of glasses and heat treatment modes in the manufacture of fiber optics. The heat capacity is also an initial characteristic in the calorimetric technique for determining optical losses in glasses.

The model-statistical approach [1] allows extrapolation in the region of low and high temperatures based on a limited set of experimental data. The model-statistical processing of calorimetric and volumetric data was used to determine the complete set of standard calorimetric and volumetric functions together with their approximation to the unexplored low-temperature region by means of parametric similarity. The use of parametric similarity of properties in the framework of the model statistical approach makes it possible to predict the standard calorimetric and volumetric functions for unexplored glasses of this series. The model parameters depend on the glass composition and allow to calculate the standard thermodynamic functions of unexplored intermediate compositions of the same series glasses.

Standard calorimetric and volumetric functions were determined using the model-statistical approach for the glass-forming system $(Ge_{0.21}Te_{0.79})_{1-x}(AgI)_x$ (x = 0.1 – 0.5) to evaluate the synthesis conditions of promising representatives of glasses $(Ge_{0.21}Te_{0.79})_{1-x}(AgI)_x$ and prediction the properties of glasses, including the functional additives that determine their optical-sensory application.

Previously experimentally determined calorimetric and volumetric data for glasses $(Ge_{0.21}Te_{0.79})_{1-x}(AgI)_x$ (x = 0.1 – 0.5) were used for physically reasonable extrapolation to the low-temperature region using a model-statistical approach.

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COMPENSATION RELATIONSHIP IN VAPORIZATION THERMODYNAMICS OF ORGANIC NON-ELECTROLYTES AND HEAT CAPACITIES OF LIQUID AND GASEOUS PHASES

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The linear relationship between Gibbs energies and enthalpies in various processes, such as solvation and vaporization, is known as the compensation relationship:

$$\Delta_l^g G^\circ = a\Delta_l^g H^\circ + b$$

Our recent research has shown that this correlation differs for for aromatic and long-chain aliphatic compounds. Previously, we identified a linear connection between the difference in heat capacities of liquid and ideal gas and vaporization enthalpy at 298.15 K, also showing differences between aromatic and aliphatic compounds:

$$\Delta_l^g C_{p,m} = a\Delta_l^g H^\circ + b$$

This study aimed to define the factors influencing the coefficients of the Gibbs energy-enthalpy correlation and explore its characteristics in aromatic and aliphatic compounds. Through thermodynamic analysis, the coefficients of the compensation relationship were determined independently, revealing dependencies on factors like the difference in heat capacities and boiling entropy.

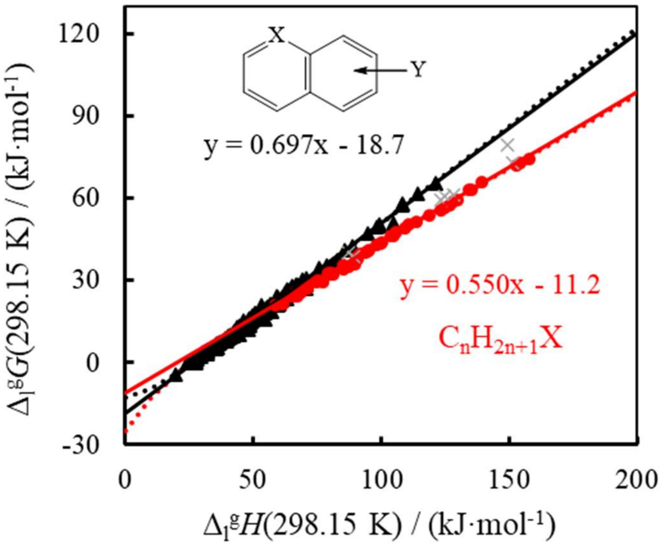

Figure 1. Graph comparison of the $\Delta_l^g G^\circ$ *vs.* $\Delta_l^g H^\circ$ correlations predicted using Trouton's rule and $\Delta_l^g C_{p,m}$ *vs.* $\Delta_l^g H^\circ$ correlation and the literature $\Delta_l^g G^\circ$ and $\Delta_l^g H^\circ$ values. Black triangles correspond to aromatic and short-chain compounds; red circles to long-chain aliphatic compounds; gray crosses to alkylarenes.

While variations in boiling entropy had minimal impact on the compensation relationship, the differing slopes seen in aromatic and aliphatic molecules were attributed to the heat capacity-enthalpy correlation.

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DEVELOPMENT OF THE COMPUTER PROGRAM FOR CALCULATION OF PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS

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Thermodynamic modelling of multicomponent systems is widely used to predict phase equilibria and diagrams. It is necessary to solve many practical problems in metallurgy, for example, optimization of technological processes. A large number of such software packages are widely used by materials scientists and industrial R&D departments (e.g., Thermocalc, Pandat, FactSage, MTDATA, OpenCALPHAD), but most of them are proprietary [1]. This makes the development of alternative solutions an urgent task, especially for the purpose of import substitution. Several years ago, such free computer programs were developed in the laboratory of chemical thermodynamics of Lomonosov Moscow State University [2]. However, they either support only up to 3-component systems (PhDi and TernAPI), or are intended only to approximate the thermodynamic properties of individual substances (CpFit). The goal of this work is to develop a more general solution capable of supporting multi-component systems and a wider range of thermodynamic models and calculation methods.

The core of the developed software provides the calculation of phase equilibria in multicomponent systems using arbitrary thermodynamic models based on Gibbs energy functions. It is implemented in the C++ language and has the following key modules:

- IRLSCPP – Contains implementation of the generalized Levenberg-Marquardt method that is used for the solution of nonlinear equations systems and robust regression.
- SUBLAT - Implementation of the sublattice model with support of internal degrees of freedom and third generation CALPHAD models.
- CONVHULL – Global minimization of Gibbs energy based on the convex hull method. It doesn’t require an initial approximation but is not very accurate.
- GIBBS - Subroutines for computation of phase equilibria in multicomponent systems based on minimization of Gibbs energy by quasi-Newtonian methods.
- DIAG - Construction of phase diagrams based on ZPF (Zero Phase Fraction) approach.
- TDB - Parser of TDB files needed for interaction with existing databases.
- API (Application Programming interface) in C++ and Lua programming languages. Lua is an interpreted language that allows interacting with the program using simple scripts.

This set of modules allows the use of a two-stage scheme for calculating phase equilibria. The first stage is an imprecise but robust estimate of the initial approximation using the convex hull method. The second is its refinement by conditionally minimizing the Gibbs energy function using a traditional method based on derivatives. Support for TDB files is important for working with existing and published thermodynamic models. TDB is the de facto standard in thermodynamic modeling publications. It is used in ThermoCalc, Pandat and MTDATA for large commercial thermodynamic databases and is accepted by international societies such as SGTE and Calphad.

The future development of the program will involve extension of supported thermodynamic models and addition of modules for optimization of model parameters.

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DETERMINATION OF ENTHALPIES OF COMBUSTION OF IONIC LIQUIDS

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The work is devoted to determining the enthalpies of combustion of some ionic liquids (ILs) using the IKA C 6000 isoperibol calorimeter. The special chemical properties of ionic liquids (high boiling points, low volatility) lead to the fact that ILs do not ignite or burn under normal conditions of a thermochemical experiment. For the first time, S.P. Verevkin et al. [1,2]. succeeded in measuring the heat of combustion of ILs.

As a result of the research, the methodology of Verevkin's experiment [1,2] on the combustion of ionic liquids in polyethylene ampoules in isoperibolic mode at a temperature of 25°C was improved and the heats of combustion of three ILs were determined - trihexyltetradecylphosphonium bromide ([P_{66614}]Br), butyltrimethylammonium bis(trifluoromethylsulfonyl)imide [4111N][NTf_2] and 1-butyl-4-methylpyridinium tetrafluoroborate [BMPy][BF_4].

The essence of our method is that to increase the accuracy of determining the heat of combustion Q, a series of experiments was carried out on the combustion of various samples of polyethylene and ionic liquids in polyethylene ampoules and the analytical dependence of Q on the mass m of samples was established.

As a result of the experiments, it was established that the heat of combustion of polyethylene and ILs increases in direct proportion to the mass of the sample. For polyethylene, in particular, as a result of processing the results of burning 9 samples in the range of 0.07888 - 0.39075 g, the following dependence of Q (kJ) on m (g) was obtained:

$$Q = 46.293\, m. \tag{1}$$

The error in determining the heat of combustion of polyethylene using equation (1) does not exceed 0.2%.

When determining the heat of combustion of ILs in polyethylene ampoules using equation (1), the contribution of the heat of combustion of polyethylene was subtracted. For 10 samples of trihexyltetradecylphosphonium bromide ([P_{66614}]Br), for example, in the sample range of 0,10985 – 0,36485 g, the dependence of the heat of combustion Q on the sample weight IL m with an error that does not exceed 0,24% is described by the equation:

$$Q = 38.944\, m. \tag{2}$$

As a result, for three ILs: [P_{66614}]Br, [4111N][NTf_2] and [BMPy][BF_4], the following combustion enthalpies were obtained, respectively: –21948±77, –6300±33 and -5935±17 kJ/mol. The values of the heats of combustion of [4111N][NTf_2] and [BMPy][BF_4] obtained in this work are comparable with similar values of the heats of combustion of 1-ethyl-3-methylimidazolium dicyanamide ([C_2MIM][$N(CN)_2$]) and 1-butyl-3-methylimidazolium ([C_4MIM][$N(CN)_2$]) [1,2]. In our case, the enthalpy of combustion of [P_{66614}]Br (–21948 kJ/mol) is significantly different, the molar mass of which is one and a half to two times greater than the molar masses of other ILs.

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The work is performed in the framework of the development program "Prioriyty-2030" of the Mendeleev University of Chemical Technology of Russia.

STUDY OF THE INFLUENCE ON THE STRUCTURE AND THERMAL PROPERTIES OF ISOVALENT SUBSTITUTION OF BISMUTH FOR EUROPIUM IN TITANATE $Bi_4Ti_3O_{12}$

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Solid solutions of the composition $Bi_{4-x}Eu_xTi_3O_{12}$ (x = 0.4; 0.8; 1.2; 1.6; 2) were prepared by the ceramic method from the initial oxides using muffle furnace and cold isostatic press. The synthesis technique is similar to described in [1].

The analysis of the phase composition of the obtained samples was carried out using powder X-ray diffraction on a D8 ADVANCE diffractometer from Bruker with a VANTEC linear detector. Figure 1 shows diffraction patterns of $Bi_{4-x}Eu_xTi_3O_{12}$ samples.

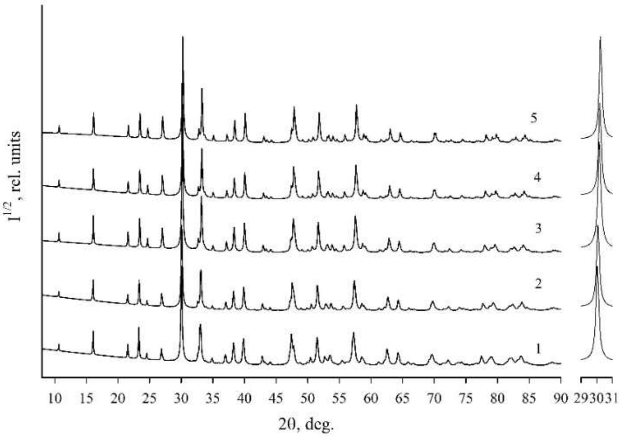

Figure 1. XRD patterns of $Bi_{4-x}Eu_xTi_3O_{12}$: 1) 0.4; 2) 0.8; 3) 1.2; 4) 1.6; 5) 2

It was found that europium-bismuth titanates with x = 0 and 0.8 are characterized by the space group *Aba*2 of the orthorhombic system. It was found that with an increase in europium concentration in samples from x = 1.2 to 2, the symmetry increases to tetragonal with the space group *P*42/*nmc*.

Using the method of differential scanning calorimetry (STA 449 Jupiter (NETZSCH, Germany)), high-temperature dependence of heat capacity Cp = f(T) has been established for samples $Bi_{4-x}Eu_xTi_3O_{12}$ (x = 0.4, 0.8, 1.2, 1.6, 2.0) in range of temperature 400-900 K.

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AN EFFUSION AND CALORIMETRIC STUDY OF SIX 5-SUBSTITUTED-1,10-PHENANTHROLINES

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The vapor pressures of six solid 5-X-1,10-phenanthrolines, whose molecular structure is given in Figure 1, were determined in suitable temperature ranges by Knudsen Effusion Mass Loss (KEML) [1].

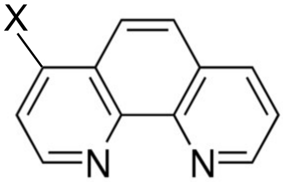

Figure 1. Molecular structure of the 5-X-1,10-phenanthrolines.
X = Cl, CH_3, CN, OCH_3, NH_2, NO_2

From the temperature dependencies of vapor pressure, the molar sublimation enthalpies, $\Delta_{g}^{cr}H_{m}^{0}(\langle T\rangle)$, were calculated at the average temperature $T=\langle T\rangle$, related to the explored temperature ranges. Since to the best of our knowledge no thermochemical data seem to be available in the literature regarding these compounds, the $\Delta_{g}^{cr}H_{m}^{0}(\langle T\rangle)$ values obtained by KEML experiments were adjusted to 298.15 K using a well known empirical procedure, available in the literature [2, 3]. The standard ($p^0 = 0.1$ MPa) molar sublimation enthalpies, $\Delta_{g}^{cr}H_{m}^{0}$(298.15 K), were compared with those determined using a recently proposed solution calorimetry approach, which was validated using a remarkable amount of thermochemical data of molecular compounds [4]. For this purpose, solution enthalpies at infinite dilution of the studied 5-chloro and 5-methylphenantrolines in benzene were measured at 298.15 K. Good agreement was found between the values derived by the two different approaches, and final mean values of $\Delta_{g}^{cr}H_{m}^{0}$(298.15 K), were recommended. Finally, the standard molar entropies and Gibbs energies of sublimation were also derived at $T = 298.15$ K. The volatilities of the six compounds were found to vary over a range of three orders of magnitude in the explored temperature range. The large difference in volatility was analysed in the light of enthalpies and entropies of sublimation. The latter was tentatively put in relation to the rotational contribution of the substituent group on the phenanthroline unit. The experimental study was complemented with a computational investigation of the gaseous molecules by a composite method approach, aimed at determining band gap energies, molecular parameters, thermodynamic functions and enthalpy changes of gas-phase reactions involving the species under exam.

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EFFECTS OF ION ASYMMETRY IN MODELING STRUCTURE AND THERMODYNAMIC PROPERTIES OF LINEAR POLYELECTROLYTE SOLUTIONS

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Theoretical description of polyelectrolyte solutions and particularly the effect of the asymmetry of the ionic charge is of great interest in modern molecular theory of solutions. The variational-field theory approach was applied by Lue [1] to extend the classical Debye-Huckel theory to ions having complex electrical structure. The Random Phase Approximation (RPA) was used by Borue and Erukhimovich [2] to describe the many-body Coulomb interactions in polyelectrolyte solutions, but only the point-charge ions were considered. In recent years, the theory has been developed systematically [3,4]; specifically, the charge distribution functions have been introduced as an input data that specifies the location of the electric charge within the ions, leading to analytical description of many complex systems within RPA.

In this work, we apply the variational field theory [3,4] to develop a model of an aqueous solution of linear polyelectrolyte chains in presence of salt where the ions may have an asymmetric distribution of the ionic charge. This model considers polyelectrolyte chains that carry charged and neutral monomers in an aqueous solution of mobile salt ions; the free energy includes the contributions from connectivity of chains, the hard-sphere excluded volume interactions, and a coulombic term obtained within RPA. The main advantage of the model is the ability to distinguish between the symmetric (such as chloride) and asymmetric (such as aminoacid anions) ions in the system, which has significant impact on thermodynamic properties and structure of solution. This approach has been successfully applied for the short-chain ionic liquid such as 1-Alkyl-3-Methylimidazolim (Cnmim, n = 4,6,8) Halides (Cl, Br).

Apart from the theoretical description of polyelectrolyte solutions, MD simulations have been performed for aqueous solutions of poly(dimethyl diallyl ammonium) salts - PDADMAX, where X=Cl-, Lys-(lysine), Leu- (leucine), or Gly-(glycine) - using GROMACS software. Full-atom model potentials (OPLS-AA force field) have been employed, treating water molecules explicitly. For selected systems, we also perform MD simulations with an implicit solvent. We examine the behavior of polycations of varying backbone length (20, 40, 60, 80, 100, 200, and 400 monomers) at 298 K. For PDADMACl and PDADMALeu systems, we perform simulations in presence of 0.5M NaCl and 0.5M NaLeu, respectively. We compare predictions from the theory with our MD data and discuss the viability of the model in reflecting the effects of the asymmetry of ions.

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MACHINE LEARNING APPROACHES FOR PREDICTING SPECTRAL CHARACTERISTICS OF VARIOUS DYES

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One of the rational approaches to solving problems associated with screening compounds in various fields of modern chemical science is through the use of artificial intelligence methods, particularly machine learning. To expedite the integration of algorithms created based on machine learning methods into a professional research environment, it is essential to have publicly available and user-friendly IT tools. Such tools may include ChemPredictor (http://chem-predictor.isc-ras.ru/), a publicly available web service developed by the G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences team (Figure 1).

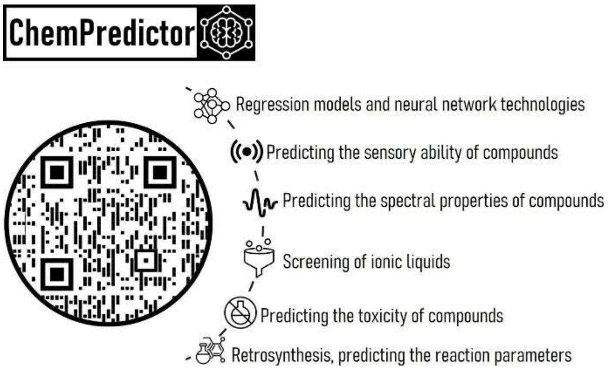

Figure 1. Functionality of the ChemPredictor web service (QR code for the main page of the web service).

Dyes of various natures serve as pillars for scientific fields such as molecular sensing, theranostics, bioimaging, and photovoltaics. Obviously, developing approaches to predict the physicochemical properties of new dyes is an urgent task, the solution of which can accelerate the targeted design of chromophores and luminophores. The report will draw the attention of listeners to the training protocol and implementation of ML models integrated into the ChemPredictor web service. These models predict the spectral properties of dyes of various natures, specifically the maximum absorption wavelength and molar absorption coefficient (http://chem-predictor.isc-ras.ru/individual/abs/) [1, 2], as well as the ^{11}B NMR chemical shift for BODIPY compounds (http://chem-predictor.isc-ras.ru/individual/nmr/) [3].

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CHROMO-FLUOROGENIC DIPYRROMETHENE CHEMOSENSORS FOR ZINC IONS DETECTION

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The development of sensors for effectively and quickly detecting ions of vital and toxic metals for humans and animals in solutions and other environmental objects is the most important task of analytical, supramolecular chemistry, biology, medicine, and environmental monitoring. Currently, according to scientists, significant progress in improving methodology of cation recognition can be achieved through the development of new highly sensitive and selective chromo-fluorogenic sensors [1- 3].

The report presents the results of testing a number of dipyrromethene ligands as chromo-fluorogenic chemosensors for the detection of Zn^{2+} ions in organic and aqueous media.

The complexation reaction of dipyrromethene ligands (HL) with $Zn(AcO)_2$ in solution is accompanied by the formation of highly stable intramolecular chelate complexes $[ZnL_2]$ and a bright, instantaneous (less than 1 minute) naked-eye coloristic response: a change in the color of the solution from lemon yellow to orange due to transition of the ligand from the molecular form to the coordinated one in the $[ZnL_2]$ composition. The chromophore response manifests itself in the absorption spectrum in the form of significant hyperchromic (2-3 fold) and bathochromic (60-75 nm) effects at the intense band maximum. Along with this, the fluorescence of the solution increases 100-200-fold, which is due to the manifestation of the CHEF effect.

To quantify the effectiveness of the sensor, the main sensor characteristics were obtained and analyzed. The sensitivity (detection limit) of spectrophotometric and spectrofluorimetric detection of Zn^{2+} ions reaches 10^{-9} - 10^{-7} mol/L. The high selectivity of the fluorescent detection of Zn^{2+} ions was confirmed by the results of comparing sensor fluorescence intensity in the combined presence of Zn^{2+} ions and background metal ions (Na^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+} and Cr^{3+}), as well as the thermodynamic constants of formation reactions of stable dipyrromethene complexes with Zn^{2+} ions and ions of a number of other metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Hg^{2+}), amounting to $\lg K^o = 7.9-10.9$ and $\lg K^o = 4.7-11.5$ respectively. The reversibility of the sensor system was assessed using competitive chelation by sequentially adding solutions of $Zn(AcO)_2$ and EDTA (as an effective chelating agent) to the sensor solution.

For the practical use of sensors for the purpose of quantitative detection of Zn^{2+} ions in aqueous media, calibration dependencies were obtained, and a methodology for express analysis was developed using test-systems based on cellulose test-strips, cotton-pads and cotton buds. Testing was successfully carried out using water samples from various natural sources.

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DESIGN OF BIFUNCTIONAL NANOSYSTEMS FOR CATALYTIC PROCESSING OF PLANT BIOMASS

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The design of bifunctional heterogeneous nanocatalysts is a rapidly developing promising area of research, since bifunctional catalysts create wide opportunities for integrating various catalytic “one-pot” processes. Thus, modern principles of "green" chemistry and sustainable development of chemical industries are being implemented. Bifunctional nanocatalysts are complex heterogeneous systems based on mono- and bimetallic metal nanoparticles immobilized on aluminosilicate supports containing Brønsted and Lewis acid sites (BAS and LAS). In the production of liquid fuel components, as well as valuable chemical "platform compounds" for fine organic synthesis based on high-molecular components of plant biomass [1], bifunctional catalytic systems can catalyze the transformation of initial substrates, excluding complex stages of isolation and purification of reaction products.

Bimetallic catalysts based on palladium and copper nanoparticles stabilized in the pores of super-crosslinked polystyrene [2] showed improved characteristics in the reaction of selective hydrogenation of furfural to furfuryl alcohol. Pd-Cu particles with an alloy structure, along with high activity, provided 100% furfural conversion and 95.2% selectivity for the target product.

In the hydrogenation reaction of levulinic acid, it was found that the use of bifunctional systems based on RuO_2 nanoparticles deposited on aluminosilicate supports of various types containing BAS and LAS on the surface makes it possible to synthesize gamma-valerolactone with a yield of 100% under mild conditions [3]. However, the strength of the acid centers is important: too high a concentration of LAS, although it allows for a noticeable acceleration of the process, at the same time leads to carbonization of the catalyst surface and a gradual decrease in its activity during reuse. Catalytic systems based on polymer supports (such as super-crosslinked aromatic polymers) [4] do not have this disadvantage. In the case of polymer catalysts, it is possible to increase the activity of the catalyst by introducing a second metal. Thus, it has been shown that Co has a positive effect on the distribution of the ruthenium-containing active phase in the pores of super-crosslinked polystyrene.

In the process of hydrogenolysis of cellulose in subcritical water, the use of Ru-containing magnetically separable catalysts, both based on organic and inorganic supports, made it possible to ensure selectivity for propylene glycol and ethylene glycol of the order of 20% at 100% substrate conversion. At the same time, the magnetically separable catalyst was characterized by better magnetization, as well as higher activity.

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CALCULATION OF THE THERMODYNAMIC PROPERTIES IN THE $SrO-TiO_2-ZrO_2$ SYSTEM BASED ON THE SEMI-EMPIRICAL APPROACHES USING THE HIGH TEMPERATURE MASS SPECTROMETRIC DATA

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The materials based on the $SrO-TiO_2-ZrO_2$ system are promising for a wide range of practical applications. For instance, the $SrO-TiO_2-ZrO_2$ ceramics is of significant interest for the development of nuclear reactor core melt traps and for modeling of the accident scenarios at nuclear power plants to prevent their consequences [1]. Moreover, the $SrO-TiO_2-ZrO_2$ system is characterized by unique electrochemical properties due to the formation of the perovskite-type phases [2] and may be used to obtain highly active solid base catalysts [3].

In the present study, the vaporization processes and thermodynamic properties of the $SrO-TiO_2-ZrO_2$ system, including the binary $SrO-ZrO_2$ and TiO_2-ZrO_2 systems, were studied by the Knudsen effusion mass spectrometric (KEMS) method [1, 4]. The samples in the system under consideration were synthesized by the solid-state method based on the $SrCO_3$, TiO_2, and $ZrO(NO_3)_2{\bullet}2H_2O$ as initial components with the maximum annealing temperature of 1723 K for at least 20 hours. The samples obtained were characterized by X-ray phase and X-ray fluorescence analyses. The KEMS study was carried out using an MS-1301 mass spectrometer at an ionizing voltage of 30 V from a tungsten twin effusion cell [4]. The vaporization of the samples of the $SrO-TiO_2-ZrO_2$ system was observed at temperatures above 1900 K, with the main vapor species being Sr, O, TiO, and TiO_2. The experimental data obtained by KEMS enabled the temperature dependences of the partial pressures of the vapor species as well as the SrO activities in the $SrO-TiO_2-ZrO_2$ system to be determined.

The thermodynamic properties in the $SrO-ZrO_2$ system described in [1], in the TiO_2-ZrO_2 system obtained in the present study, and in the $SrO-TiO_2$ system derived earlier [5] allowed the excess Gibbs energies in the $SrO-TiO_2-ZrO_2$ system to be calculated by the semi-empirical Kohler, Toop, Redlich-Kister, and Wilson methods. The excess Gibbs energy values calculated in the system under study showed negative deviations from the ideal behavior at the temperature 2100 K. The calculated values of the SrO и TiO_2 activities were compared with the experimental data, demonstrating a reasonable agreement. Discrepancies between the results obtained using various semi-empirical methods were discussed.

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NEAR-INFRARED SPECTROSCOPY AS AN EFFECTIVE TECHNIQUE TO STUDY CONFORMATIONAL EQUILIBRIA OF LIDOCAINE MOLECULES IN A HIGHLY CONCENTRATED LIDOCAINE SOLUTION IN SUPERCRITICAL CO_2

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In this work, we applied near-infrared spectroscopy to study conformational equilibria of lidocaine molecules in a highly concentrated lidocaine solution in $scCO_2$ (at the CO_2 density ranging from 1.5 to 2.0 of its critical value). Lidocaine was chosen as the study object because it has higher solubility in $scCO_2$ over a wide phase diagram range than most other pharmaceuticals. This fact suggests that intermolecular hydrogen bonds may be formed between lidocaine molecules due to the steric factor. In turn, the specific intermolecular interactions may affect the conformational equilibria of lidocaine molecules as well as the distribution of intramolecular hydrogen bonds. Near-infrared spectroscopy offers significant advantages over mid-infrared spectroscopy when studying hydrogen bonding, as it enables more precise differentiation of spectral contributions of vibrations of free functional groups and groups involved in both intra- and intermolecular hydrogen bond formation.

To achieve the intended goal, we measured the evolution of the IR spectra of lidocaine dissolved in $scCO_2$ under isothermal compression conditions within the pressure range of 100–300 bar at a temperature of 35°C. Then, we analyzed the $2\nu_s$(N–H) spectral band, which corresponds to the first overtone of the lidocaine molecule N–H fragment stretching vibration. This particular spectral band was selected for analysis because the N–H fragment of the lidocaine molecule can participate in both intra- and intermolecular hydrogen bonding. In our analysis, we used the results of our recent work [1], in which we applied a combination of chemometric approaches and quantum-chemical calculations to study the evolution of the ν_s(N–H) spectral band for a diluted lidocaine solution in $scCO_2$ at a constant lidocaine concentration within the same phase diagram range. Our findings revealed a significant increase in the likelihood of intermolecular hydrogen bond formation caused by lidocaine concentration growth. This resulted in greater population of lidocaine molecules without an intramolecular hydrogen bond.

Furthermore, through the analysis of the ν_s(N–H) and $2\nu_s$(N–H) spectral bands for both diluted and concentrated solutions, we determined that the key factor influencing the formation of intermolecular hydrogen bonds in lidocaine solutions in $scCO_2$ is the lidocaine concentration rather than pressure. We also identified the lidocaine concentration threshold in the solution, at which the proportion of molecules involved in intermolecular hydrogen bonding becomes statistically significant. This threshold concentration value lies within the range of $1–1.4\cdot10^{-1}$ mol/L and can be achieved at 35°C when the $scCO_2$ density reaches 1.5 – 1.6 of its critical value.

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INFLUENCE OF UNCERTAINTY OF PHASE MODELS' PARAMETERS OF BINARY Au–Pd ON CALPHAD CALCULATION OF THE Au–Ag–Pd TERNARY

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Thermodynamic modeling allows to reduce time and material costs for the study of phase equilibria in multicomponent systems. To improve the reliability of predicting the phase composition and properties of phases, it is important to estimate the uncertainty of the parameters of CALPHAD models. The uncertainty of model parameters is due to various factors: the lack of experimental information to unambiguously determine the model parameters, the errors in the experimental data, as well as the uncertainty of the models themselves. The purpose of this study was to quantify the uncertainty of model parameters of fcc and melt in the binary Au–Pd and investigate its influence on the calculations of phase equilibria in the Ag–Au–Pd ternary.

The liquidus and solidus temperatures, as well as the heats of melting of 6 alloys of the Au–Pd system, were determined by the DTA/DSC method. These results, together with the published data, were used to make a new thermodynamic description of the system. The emphasis was placed on new results of measurements of the solidus temperature and melting enthalpies by proper adjusting of data weights. The new assessment of Au–Pd system shows good agreement with both our and literature data. In particular, it does not exhibit the extremely unusual behavior of the calculated thermodynamic properties of the melt - a change in the sign of the excess Gibbs energy in the composition region near Pd, which was observed in previous calculations.

The statistical jackknife method was used to estimate the uncertainties of phase model parameters obtained from the CALPHAD calculation of the Au–Pd system. Using the "probing" method, we assessed the influence of estimated uncertainty in the parameters of the fcc and melt models on the calculation of the corresponding equilibria in the ternary Ag–Au–Pd. To implement this approach, macros were prepared in the Thermo-Calc package. However, due to the very high labor consuming of this method, which involves repeating calculations with varying parameter values within appropriate limits, only 3-5 test points could be used during "probing" and calculations were performed only for a limited number of compositions and/or temperatures.

By "probing" the uncertainty region of parameter values, the uncertainty of the calculated coordinates of phase equilibria in the Ag–Au–Pd system was estimated, which was approximately 0.02 mole fraction in composition and 5 K in temperature. Thus, in the studied ternary system, the scatter of the calculation results does not exceed the discrepancy between the various results of studying the bounding Au–Pd system.

In addition, the fundamental need to take into account the mutual correlation of the phase model parameters obtained during optimization has been confirmed. In particular, the coefficients of the temperature dependence of the interaction parameters of both phases turn out to be nearly linearly depended: the modules of the correlation coefficients were 0.998-0.999 and more. This was also confirmed by the "probing" of areas of uncertainty, when any attempt to independently vary the enthalpy and entropy contributions to the interaction parameters leads to a sharp deterioration in the results.

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THERMODYNAMIC ESTIMATION OF THE PHASE AND CHEMICAL EQUILIBRIA IN THE SYSTEMS Al – Mg – Si – O AND Al – Mg – Si – H_2O

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In the automotive and aeronautics sectors, aluminium and magnesium are among the lightest structural metals with a wide range of alloys based upon them. However, atmospheric and aqueous corrosion is very easy to affect aluminum and magnesium and, therefore, the alloying elements should improve their corrosion resistance. In this work, the thermodynamic analysis of phase and chemical equilibria involving aluminum and magnesium alloys doped with silicon in excess oxygen, as well as the analysis of chemical and electrochemical equilibria involving these alloys in aqueous environments is conducted.

The phase and chemical equiliibria in the Al–Mg, Al–Si, Mg–Si, and Al–Mg–Si systems at 298 K are considered using the software MatCalc. The solid solubility of the alloy components is estimated, the thermodynamic activities of the components of common Al–Mg–Si system alloys are calculated, the standard Gibbs energies of formation of intermetallic phases $Al_{140}Mg_{89}$, $Al_{12+k}Mg_{17-k}$ ($0 < k < 0.284$) and Mg_2Si are collected.

The standard Gibbs energies of formation of various simple and mixed oxides and hydroxydes of aluminium, magnesium and silicon, including corundum, periclase, quartz, Al-Mg spinel, kyanite, mullite, forsterite, clinoestantite, cordierite, sapphirine, kaolinite, pyrophilite, chrysolite, talc, anthophylite, sepiolite, chlorite, saponite, palygorskite and montmorillonite were collected. The invariant chemical equilibria in the systems Al–Mg–O, Al–Si–O, Mg–Si–O at 298 K are considered, the isothermal section of the state diagrams of these systems are plotted, and the oxidation scheme of the Al–Mg–Si system alloys in excess oxygen is proposed. The stability of different polymorphs of aluminium and magnesium oxides, hydroxides and silicates is determined.

The thermodynamic data on the aqueous species of aluminium, magnesium and silicon are collected. The chemical and electrochemical equilibria in the Al–Mg–Si–H_2O system at 298 K are considered and presented in form of the activity – pH and the potential – pH diagrams, and the oxidation of the Al–Mg–Si system alloys in aqueous environments is determined.

The complexity of the corrosion behaviour of the systems Al–Mg–Si–O and Al–Mg–Si–H_2O resembles the complexity of the equilibria describing the formation of clay minerals in the Earth’s crust. Moreover, the presence of aluminum and magnesium hydrides drastically changes the oxidation mechanism and the corrosion properties of Al–Mg–Si alloys.

The extreme complexity of the system and the similarity of the thermodynamic properties of different mixed oxides and hydroxides lead to the fact that thermodynamics alone does not provide an exhaustive answer to the question of the mechanism and the products of the Al–Mg–Si alloys corrosion. The corrosion properties of the specific alloys in a specific environment are determined by the precipitation kinetics and the mechanical properties of the formed oxides. The knowledge of the chemical and electrochemical equilibria in the system and of the possible formed oxidation products opens the way to the study of the physical, chemical and mechanical properties of the passivation films formed on the alloy surface. the present thermodynamic calculations might be a useful starting point for the subsequent complex evaluation of the corrosion behaviour of aluminum–magnesium–silicon alloys.

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BODIPY PHOTOSENSITIZERS DELIVERY SYSTEMS: STRUCTURAL AND PHOTOPHYSICAL PROPERTIES

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The design of biocompatible photosensitizers with optimal combination of intense fluorescence and singlet oxygen generation is complex and urgent task. Boron(III) dipyrromethene dyes (BODIPYs) are biocompatible, photostable luminophors with excellent accumulation in cancer cells, as well as pronounced activity against various types of pathogenic microorganisms.

Two key methods of molecule functionalizing are used to obtain BODIPY photosensitizers (PSs): 1 - the “heavy atom effect” strategy, i.e. introduction of heavy halogen atoms into dye molecules; 2 - oligomerization, i.e. obtaining halogen-free bichromophore PS with a predominantly orthogonal structure. A number of bromo- and iodine-substituted monochromophores, as well as non-halogenated bis(BODIPY) bichromophores, were synthesized in our research group, the structural and solvation effects on their photophysical and photochemical characteristics were analyzed in detail, and leading compounds with an optimal combination of intense fluorescence and $^1O_2$ generation were identified. The BODIPY high hydrophobicity and tendency to aggregate require the selection of biocompatible delivery systems to ensure their functionality in physiological environments. That's why, we have obtained two types of BODIPY PS nanoscale delivery systems: water-stable pH-controlled BODIPY@ZIF-8 based on zeolitic imidazolate frameworks and water-soluble bis(BODIPY)@Pl based on Pluronic® F127 polymeric micelles. The sizes of the resulting supramolecular systems and the dye spectral characteristics in their composition are determined by the luminophor and delivery chemical structures, the size of ZIF-8 pores or Pluronic micelles hydrophobic core, as well as the conditions for the dye encapsulation. It has been established that bromine-substituted BODIPYs are effectively encapsulated in the pores/cavities of ZIF-8, in contrast to non-halogenated bichromophores. The optimal method for encapsulating Br-BODIPYs into ZIF-8 is a simple nanoprecipitation process during MOF synthesis using methanol or tetrahydrofuran solutions. As a result, intensely fluorescent BODIPY@ZIF-8 nanoparticles were obtained, demonstrating effective dye release in phosphate buffer (PBS) suspension with pH ≤ 6.5. The efficiency of non-halogenated BODIPY bichromophores solubilization by Pluronic micelles, on the contrary, is higher compared to bromine-substituted monochromophores. Using the thin film method, water-soluble forms of halogen-free bis(BODIPY)@Pl PSs were obtained, demonstrating effective chromophore, fluorescent and $^1O_2$ generation characteristics in PBS (pH 7.4).

The obtained results provide valuable insights for further research on the use of the BODIPY@ZIF-8 and bis(BODIPY)@Pl in photodynamic therapy (PDT) and antimicrobial photodynamic therapy (APDT).

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VAPORIZATION AND THERMODYNAMIC PROPERTIES OF $La_2Zr_2O_7$, $Nd_2Zr_2O_7$ AND $Eu_2Zr_2O_7$ STUDIED BY KNUDSEN EFFUSION MASS SPECTROMETRY

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The refractory properties of the Ln_2O_3-ZrO_2 system are considered promising for production of a great deal of high-temperature materials, e.g., thermal barrier coatings and casting molds for the gas turbine engine blades. At high temperatures components of the Ln_2O_3-ZrO_2 system may vaporize selectively which may change significantly physicochemical properties of the materials. Therefore, information on vaporization processes and thermodynamic properties of the Ln_2O_3-ZrO_2 system is of great importance. In the present study, the temperature limits of thermal stability and the nature of vaporization of lanthanum, neodymium and europium zircons are established. Thermodynamic properties of $La_2Zr_2O_7$ (s), $Nd_2Zr_2O_7$ (s), $Eu_2Zr_2O_7$ (s), as well as solid solutions of Nd_2O_3-ZrO_2 and Eu_2O_3-ZrO_2 systems at high temperatures were determined. The work was performed using the Knudsen effusion mass spectrometry on the MS-1301 mass spectrometer at an ionizing voltage of 25 V. Samples were evaporated from a twin Knudsen effusion cell heated by electron bombardment. In one of the compartments of the cell, the studied zirconate was loaded, and in the second, comparative, individual lanthanum, neodymium or europium oxide. The temperature was measured with an optical pyrometer EOP-66 with an accuracy of ±10 in the temperature range 1727-2427 ^{0}C. The appearance energies (AE) of ions were measured by the vanishing current method with ±0.3 eV error using gold as an energy standard. Instrument calibration was performed using the calcium fluoride. The partial pressures of LaO, NdO, EuO and atomic europium were determined by comparing ion current method.

It was shown that at temperatures 1875-1994 ^{0}C the main vapor species over the $Nd_2Zr_2O_7$ were NdO and atomic oxygen O. The main gaseous species over $La_2Zr_2O_7$ and $Eu_2Zr_2O_7$ in the temperature range 2006-2332 and 1697-1942 ^{0}C respectively were LaO (EuO), atomic La (Eu) and O. The second component of the systems ZrO_2 transferred into the vapor in the form of ZrO_2, ZrO and atomic oxygen O at temperatures higher than 2227 ^{0}C.

It is established that the evaporation of lanthanum, neodymium and europium zirconates can be described by equations:

$Ln_2Zr_2O_7$ (s) = LnO (g) + O (g) + 2 ZrO_2 (s)
$Eu_2Zr_2O_7$ (s) = 2 Eu (g) + 3 O (g) + 2 ZrO_2 (s)
Ln = La, Nd, Eu.

The data obtained by us allowed us to calculate the values of the standard enthalpy of formation of lanthanum, neodymium and europium zirconate, as well as the enthalpy of formation of these compounds from the corresponding solid oxides.

The use of a twin effusion cell made it possible to determine the activity values of Ln_2O_3 in the condensed phase. The dependences of the activity values of Nd_2O_3 and Eu_2O_3, as well as La_2O_3 in the regions of pyrochlore existence correlate with the phase diagrams of the Ln_2O_3-ZrO_2 systems. The activity values of lanthanum, neodymium and europium oxides are constant in the area of the phase diagram in the region of pyrochlore existence. The values of Ln_2O_3 activities gradually decrease during the transition from the pyrochlore region to the fluorite-type solid solution region. In the studied systems, there is a significant negative deviation from the ideal behavior.

A NEW LOOK AT THE PHASE EQUILIBRIA IN TERNARY SYSTEMS COMPOSED OF SEMICRYSTALLINE POLYMER, SOLVENT AND NONSOLVENT

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Ternary mixtures of a semicrystalline (SC) polymer with a solvent and a nonsolvent are widely used primarily for preparation of membranes by nonsolvent induced phase separation (NIPS). A detailed analysis of the published studies devoted to phase equilibrium in such systems showed that the phase diagrams were either incomplete or presented in a schematic form. In the report we propose a new method of plotting the ternary phase diagrams for the SC polymer – solvent – nonsolvent mixtures. This method is based on finding the location of the isotherm intersection with the curves on the temperature–composition pseudobinary phase diagrams for the SC polymer mixtures with solvent and binary mixtures of solvent and nonsolvent of different composition. The coordinates of the intersection points were used to plot for the first time the complete ternary phase diagram for the widely used mixture of polyvinylidene fluoride (PVDF) with dimethyl acetamide (DMAc) and water. The curves on the phase diagram separate the regions of homogeneous mixtures (yellow), coexistence of two liquids (red), macroscopically uniform gels (swollen SC polymer) (blue) and coexistence of such gels with liquid (green).

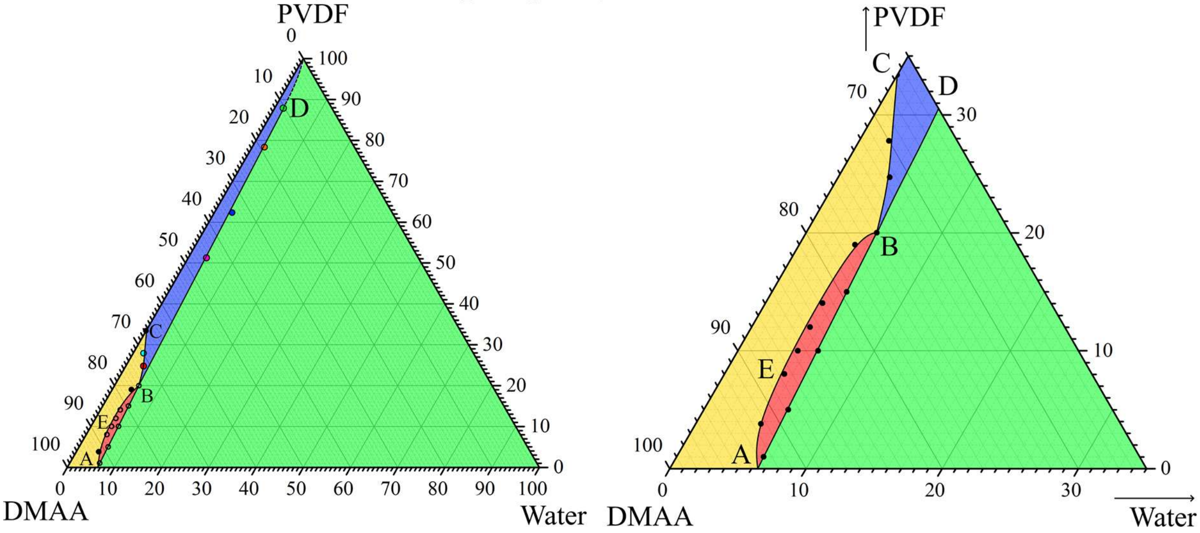

Figure 1. Ternary phase diagram for the PVDF – DMAc – water system at 60°C (left) and its lower left corner enlarged (right).

Using the plotted phase diagram, a new understanding of the NIPS mechanism was proposed and confirmed by direct microscopic observation of the NIPS process and SEM analysis of the membranes obtained following this way. An unexpected result of the study is discovery of the crystalline complexes in the mixtures of PVDF and DMAc, which was confirmed using both DSC and XRD techniques.

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SPATIAL STRUCTURE OF FENAMATE MOLECULES IN LIPID BILAYERS: INSIGHTS FROM MAS NOESY

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Penetration, localization and distribution of molecules in the lipid membrane bilayer are steps preceding drug binding to protein. The mutual influence of membrane molecules and drugs largely determines the characteristics of the spatial structure of the molecules, which in turn affects the binding processes [1]. Drug molecules can take on various conformations due to the constantly changing structure of lipid membranes, with low transition barriers between them [2]. This situation creates an ideal environment for effectively adapting drug compounds in the lipid bilayer [3]. An analysis of the literature showed that there are few studies aimed at quantitatively assessing the characteristics of the spatial structure of small molecules in the lipid bilayer due to the need for special physicochemical tools for solving such problems. In this work, an approach based on nuclear Overhauer effect spectroscopy with magic angle spinning of a sample (MAS NOESY) is used to determine the proportions of groups of conformers of fenamate molecules (mefenamic, tolfenamic and flufenamic acids) in the environment of a model lipid membrane of phosphatidylcholine (POPC). A set of probable conformers of the fenamates differing in the value of the dehydral angle C2-N(H)-C3-C7 was determined based on quantum chemical calculations. A study was conducted to calculate the distances between the nuclei of fenamates in different conformations. The study also assessed the proportions of different groups of conformers (see figure 1) and compared the results with previous studies on the spatial structure of the objects of study in a solution. Within the experimental error, the proportions of the A+C and B+D conformer groups of MFA and TFA were comparable. The error in determining distances in the experiment was accounted for, which reached 2–3%. In NOESY experiments, these conformer groups were indistinguishable and amounted to approximately 47.8 % / 52.2 % and 47.7 % / 52.3 % for MFA and TFA, respectively. [2]. For MFA and TFA, the preferred conformation observed was B+D, whereas for FFA, it was A+C. This indicates a difference in the preferred conformational states among the fenamate compounds studied. The approach and results of this study [4] provide valuable information that can help improve the process of modifying drug compounds.

Figure 1. Chemical structure and distribution of fenamates conformers.

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THERMAL BEHAVIOR OF IONIC LIQUID/ALUMINOSILICATE IONOGELS

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In recent decades, significant research attention has been paid to the development of synthesis methods and the study of the properties of ionogels - hybrid materials based on ionic liquids (ILs), which are salts consisting of a large organic cation and an organic or inorganic anion and melting at a temperature of <100°C. Composites containing ILs and clay minerals are chemically inert, have low vapor pressure and high electrical conductivity (which is characteristic of ionic liquids), and, at the same time, have lower fluidity compared to the original IL.

Two-component ionogels containing clay minerals such as montmorillonite K10 (Mnt-K10), bentonite (Bent), and halloysite (Hly), as well as imidazolium-based ionic liquids (ILs) were prepared in present work. The ILs that were used in the synthesis included a bis(trifluoromethylsulfonyl) imide anion ($TFSI^-$) and various cations: 1-ethyl-3-methylimidazolium ($EMIm^+$), 1-propyl-3-methylimidazolium ($PMIm^+$), 1-butyl-3-methylimidazolium ($BMIm^+$), and 1-butyl-2,3-dimethylimidazolium ($BDMIm^+$).

The thermal behavior of the synthesized materials was studied using differential scanning calorimetry (DSC) and thermogravimetry (TG) in an argon atmosphere. The results obtained are shown in Figures 1 and 2.

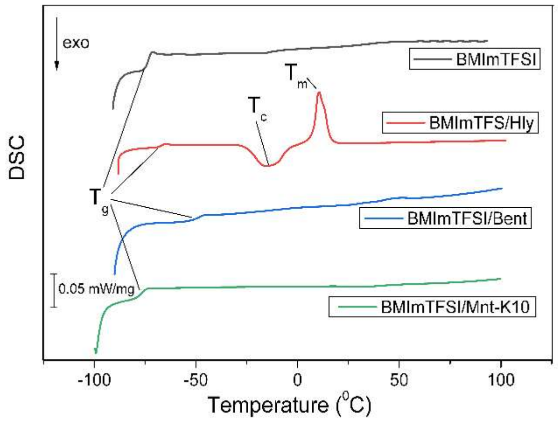

Figure 1. DSC traces of the second heating cycle recorded for ionogels containing BMImTFSI

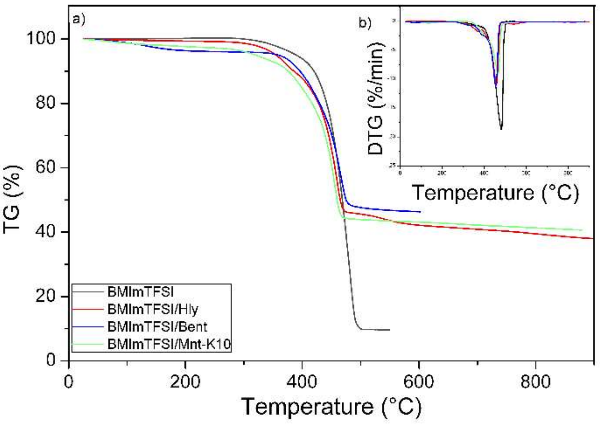

Figure 2. TG (a) and DTG (b) traces recorded for ionogels containing BMImTFSI

It was found that the ionogels had higher glass-transition temperatures compared to the corresponding ILs (without clay filler). In addition, the characteristic temperatures of thermal decomposition of clay-entrapped ILs were lower than those for pristine ILs. It was assumed that the identified differences in the thermal behavior between the pristine and clay-entrapped ILs (confinement effect) are associated with an increased role of ion-wall interactions compared to ion-ion interactions.

A DATA-DRIVEN APPROACH TO DESIGNING DEEP EUTECTIC SOLVENTS AS EFFICIENT CO_2 ABSORBERS

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The effective management of CO_2 is crucial for the development of sustainable technologies. Currently, the most widely used method to reduce CO_2 emissions is carbon capture, utilization, and storage (CCUS). However, traditional amine-based absorbents, which have been used for many years, face various technological issues such as corrosion, sorbent degradation, and high energy consumption for regeneration. Therefore, there is a need to develop new and more eco-friendly CO_2 absorbers.

Ionic liquids (ILs) have been extensively researched as potential solvents for CO_2 capture. However, their complex synthesis and purification processes make ILs expensive. As an alternative, deep eutectic solvents (DES) have emerged as a promising option for CO_2 capture. DESs are solutions consisting of Lewis or Brønsted acids and bases, known as hydrogen bond donors (HBDs) and acceptors (HBAs), which form a eutectic mixture. The initial components of DES form a network of hydrogen bonds, leading to a significant decrease in melting temperature compared to the individual compounds. By adjusting the components and their ratios, it is possible to create DESs with the desired CO_2 absorption capacity.

The study aimed to use virtual screening to identify new combinations of compounds that can absorb CO_2. Machine learning models were initially created to predict CO_2 uptake in DES. To diversify the chemical structures used in the model training, the sample was expanded to include data on CO_2 solubility in ILs. Additionally, machine learning regression models were developed to predict the parameters of the Redlich-Kister equation for calculating the melting temperature of new compound combinations of DES. These models were then used for multilevel screening of potential absorbents. The proposed methodology, involving computational experiments, is expected to yield new DESs with high CO_2 absorption capacity, liquid at room temperature, and with low viscosity. All developed models are publicly available and can be accessed online at http://chem-predictor.isc-ras.ru/ionic/des.

The financial support of the work was provided by the Russian Science Foundation № 23-13-00118, https://rscf.ru/project/23-13-00118/

TWO-CHANNEL DYE BASED ON BODIPY-CYANINE 7.5 CONJUGATE

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Boron(III)dipyrromethenates (BODIPY) are a class of luminophores known for their unique, easily configurable physicochemical (including spectral) properties. Today, there are a large number of approaches to BODIPY functionalization for use in various scientific fields, one of which is the conjugation of BODIPY with other fluorophores. The conjugates produced in this way have a wide range of desired spectral properties, including the red shifting emission maxima position and the ability to generate singlet oxygen. The product of the conjugation reaction may also be able to absorb and/or emit light simultaneously at several different wavelengths, allowing it to be used to obtain more comprehensive information about biological objects and systems. This is particularly useful for multiplexing – the simultaneous detection of multiple analytes in a sample. In this regard, the primary objective of the investigation was to develop a new BODIPY-cyanine 7.5 conjugate as a probe with a ratiometric spectral signal in the green and near-infrared spectral regions (Figure 1).

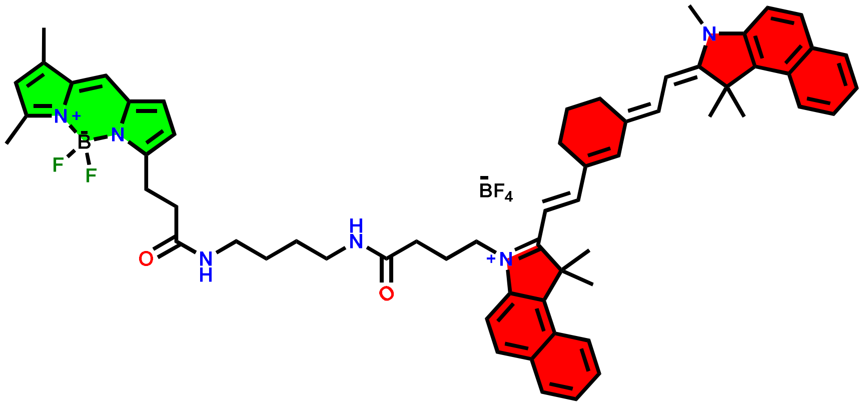

Figure 1. Structure of BODIPY-cyanine 7.5 conjugate.

The report presents the results of synthesis, identification, experimental, and computer studies of the physicochemical properties of the new BODIPY-cyanine 7.5 conjugate. The absorption and emission spectra of the conjugate are characterized by the presence of two bands with maxima in the green and NIR spectrum regions, corresponding to the BODIPY and cyanine 7.5 characteristic absorption bands maxima, but red-shifted. The spectral characteristics of the BODIPY-cyanine 7.5 conjugate turned out to be very sensitive to the properties of the solvating medium, which may be attributed to the presence in the molecular structure of the conjugate of a large number of centers for specific solvation by solvent molecules in both the ground and excited states. Special attention is paid to the practical applications of the BODIPY-cyanine 7.5 conjugate in confocal fluorescence microscopy. This is due to the fact that traditionally, two dyes are used to observe cells in the red and green regions, whereas in this case, one conjugate suffices. The advantage of the conjugate is that using two dyes may cause signal overlap, whereas the conjugate signals do not overlap.

THE SECOND BEGINNING AND CURRENT STATE OF THERMODYNAMICS

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Thermodynamics is a field of knowledge without model concepts [1-3]. It includes: (1) the basic principles, first and second Beginnings of thermodynamics, (2) the combined form of these records in the form of thermodynamic potentials, (3) consequences from these two Beginnings, which are expressed in the form of the first and second derivatives from the selected thermodynamic potentials along natural variables.

The second Beginning of thermodynamics is expressed by R. Clausius's inequality $\delta S \geq \delta Q / T$ (where S is the entropy, δQ is the amount of heat, T is the absolute temperature) [1]. Clausius's formulation of the second Beginning of thermodynamics is complex. It simultaneously reflects: 1) the process of striving in a closed system to achieve equilibrium, and 2) this limiting state of equilibrium itself [4,5]. The transition from nonequilibrium states with an internal energy $dU_{ne} < TdS - PdV$ to the equilibrium state $dU_e = TdS - PdV$ is described by kinetic equations [5]. Near equilibrium, processes of relaxation of thermodynamic parameters occur, characterizing the processes of transition of the system to an equilibrium state. In experiments the following relationships are always (excluding rarified gas) satisfied between the relaxation times of the processes of transfer for momentum (τ_P), energy (τ_T) and mass (τ_{mas}): $\tau_P \ll \tau_T \ll \tau_{mas}$ [3-6].

Gibbs took as a basis the equation $dU_e = TdS - PdV$ for equilibrium states [2], with limiting values of mathematical functions with time dependence at $t \to \infty$, when complete equilibrium of the system is achieved. This entry corresponds to the choice of a quasi-static process as the main process of thermodynamics, excluding all time of relaxations.

The lecture demonstrates the influence of the difference between the interpretations by Gibbs and Clausius of the second Beginning of thermodynamics on:

1. five types of surface characteristics of dispersed, small and limited systems. All existing surface characteristics and dispersed phases: surface tensions, contact angles, disjoining pressure, properties of small systems, cannot be correctly formulated and calculated without the use of information on experimental data on relaxation times processes of transfer of momentum, energy and mass.
2. a state of a solid. When solids are in equilibrium, the presence of stress components is impossible.
3. methods of statistical physics in the theory of the liquid state, which do not take into account the vibrational movements of molecules, and for calculating surface characteristics;
4. methods for calculating rates and equilibria of chemical reactions in non-ideal media (supercritical fluids as well as combined phase and chemical equilibria at subcritical temperatures), and other corrections of the existing thermodynamical interpretations.

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THE EVAPORATION STUDY AND THERMAL STABILITY OF SOME IMIDAZOLIUM-BASED IONIC LIQUIDS

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Ionic liquids (Ils) are the hot topic in the last decades. The unique physicochemical properties of these compounds, such as low volatility, non-combustibility and resistance to many chemical agents, offer a tantalizing perspective. The Ils was applied as a solvents, catalytic environment, lubricants and heat-transfer agents. Unfortunately, information about thermodynamics and thermostability data of Ils often is not available. But reliable information about thermodynamics properties is needed to predict the properties of ILs in different application and useful for the development of the theory of liquid phase.

In this study, the determination of thermodynamic parameters of evaporation of the following Ils: [EtMIm][MS], [BuMIm][MS], [EtMIm][Cl], and [BuMIm][Cl] was carried out. The thermodynamics information about evaporation of methanesulfonates, [EtMIm][MS] and [BuMIm][MS], such as saturated vapor pressure and enthalpy of vaporization $\Delta_{vap}H_T^0$ was presented in the literature fragmentally [1,2]. The information about their thermal stability is not available. The determination of vapor pressure and $\Delta_{vap}H_T^0$ was carried out by the method of Knudsen effusion mass-spectrometry (KEMS). Commercial MI1201 magnetic mass spectrometer (r = 200 mm, R = 500) with original high temperature ion source (EI, E_{ion} = 70 eV) was used. The $\Delta_{vap}H_T^0$ was determined by "Second Law Treatment" and "Third Law Treatment" procedures. To calculate the thermodynamic functions of liquid state the heat capacities of ionic liquids were obtained by high vacuum calorimetry. Thermodynamics functions of ideal gas state were calculated with quantum chemistry methods. Under the KEMS conditions, [EtMIm][MS] and [BuMIm][MS] are not thermally stable. In the case of [EtMIm][MS] the quantitative description of the thermolysis process was carried out. The kinetic curves for thermolysis reactions were obtained and the pseudo-zero order regions were found. The thermolysis proceeds by a typical S_N2-mechanism. The possible products of [BuMIm][MS] thermolysis were described. The thermodynamic activity of both methanesulfonates is equal 1 under the experiments: MALDI and APCI mass spectra of initial samples and residues in the cells after evaporation were similar.

The evaporation study of chlorides, [EtMIm][Cl] and [BuMIm][Cl], was presented early[3,4]. In this work, the thermostability and chemical transformation of [BuMIm][Cl] have been investigated more thoroughly. It was found that in addition to the thermolysis of [BuMIm][Cl] by the S_N2-mechanism, a new ionic liquid [BMMIm][Cl] was formed by the C2-methylation of [BuMIm][Cl]. The methylating reagent is chloromethane formed by [BuMIm][Cl] thermolysis.

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NOVEL WATER-SOLUBLE FORMS OF RED-EMITTING BODIPY LUMINOPHORES BASED ON PLURONIC F127: SPECTRAL, STRUCTURAL CHARACTERISTICS AND APPLICATION POSSIBILITIES IN BIOIMAGING

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Luminescent dyes are used in medicine to diagnose and treat various diseases, including cancer. Fluorescence is particularly important for biomedical applications in the near red region of the spectrum, the so-called "phototherapeutic window", as it is characterised by a deeper penetration of light into tissues. Especially interesting are BODIPY-based organic dyes, which have a unique combination of physical and chemical properties. Structural functionalisation allows to shift the absorption and fluorescence spectra for practical applications.

However, due to their high hydrophobicity, most BODIPY dyes aggregate in solutions with high water content, including physiological media, which limits the use of dyes for biomedical purposes.

Using Pluronics to increase the solubility of the dyes is a resolution to the problem. Pluronics are bi-functional amphiphilic polymers having two hydrophilic (ethylene oxide) blocks and a hydrophobic (propylene oxide) middle part. They form micelles of different morphologies and thus contribute to the efficient use of dyes in the study of biological systems.

The aim of the study is to obtain and study the spectral characteristics of a series of red-emitting styryl- and pyrrolyl-BODIPY luminophores in solutions of organic solvents of different polarity and in aqueous suspension of Pluronic F-127 micelles, as well as to investigate their biological activity and biocompatibility. The following tasks were solved:

1) study spectral characteristics of BODIPY dyes in different nature solvents;

2) encapsulation of luminophores in micelles of amphiphilic block copolymer Pluoronic® F-127;

3) investigating the BODIPY@Pluoronic spectral characteristics and micellar particle sizes in the PBS buffer (pH 7.4):

4) study of biocompatibility of the BODIPY@Pluoronic micellar suspension

Obtained BODIPY and BODIPY@Pluoronic are demonstrating intense absorption and fluorescence in the near-infrared region of the spectrum (from 650 to 750 nm). Solubilisation efficiency is high and accounted from 70 to 80%. Analysis of the obtained BODIPY@Pluoronic systems size showed that with increasing concentration of solubilised dye, increase of particle size from 140 to 300 nm was observed.

All blood samples with the addition from 1 to 100 μg/ml of BODIPY@Pluoronic at 1 and 3 hours were found to contain less than 1% spontaneous haemolysis and therefore not erytotoxic.Concentration of BODIPY@Pl systems not to affect ADP-induced platelet aggregation. Analysis of micelles effect on survival of human dermal fibroblast cell line showed that they were not cytotoxic.

The obtained results allow us to recommend water-soluble BODIPI@Pl systems for further studies on their application as biomarkers for disease diagnostics.

SOLUBILITY THERMODYNAMICS AND PERMEABILITY OF RILUZOLE WITH CYCLODEXTRINS AND POLYMERS

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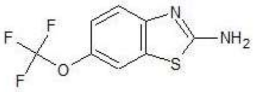
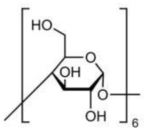
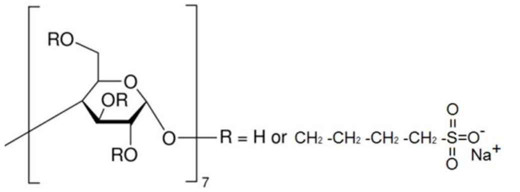
Riluzole (RLZ) - a sodium channel-blocking benzothiazole anticonvulsant drug was approved by Food and Drug Administration in 1995 for the treatment of amyotrophic lateral sclerosis [1]. The effect of riluzole is derived from its ability to block glutamate release and enhance glutamate reuptake leading to the inhibition of glutamate-dependent signaling [2]. Riluzole is considered as a very slightly soluble compound at pH 6.8 (phosphate buffer) which can be crucial for permeability through the membranes and absorption, thereby limiting application. To improve aqueous solubility and modulate dissolution rate and membrane permeability, complex formation of RLZ with two cyclodextrins: α-cyclodextrin (α-CD) and sulfobutylether-β-cyclodextrin (SBE-β-CD) was studied.



RLZ



α-cyclodextrin(α-CD)



sulfobutylether-β-cyclodextrin(SBE-β-CD)

The stability constants of RLZ/α-CD and RLZ/SBE-β-CD were determined to be 102.27 M^{-1} and 1103.56 M^{-1} at 310.15 K demonstrating a greater affinity of RLZ towards SBE-β-CD than α-CD. This result was attributed to the more suitable hydrophobic cavity and to an additional hydrophobic region near the cavity of SBE-β-CD composed of only the alkyl ether moieties of the sulfobutyl groups. In buffer pH 6.8 in the solutions of 1% cyclodextrins the 1.7-fold and 3.7-fold solubility growth with α-CD and SBE-β-CD, respectively, was detected and accompanied by the reduction of the permeability. The experiments on the equilibrium solubility and membrane permeability (cellulose membrane MWCO 12-14 kDa) under static solubilizing conditions carried out for RLZ in the solutions of 1% cyclodextrins with the additions of 1% polymers (polyethylene glycol 400, polyethylene glycol 1000, propylene glycol, hydroxypropyl methyl cellulose and polyvinylpyrrolidone) revealed the most advantageous three-component systems in view of solubility-permeability interrelation. The dynamic dissolution-permeation experiments for solid RLZ/CD complexes were carried out for comparison with untreated RLZ.

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DICLOFENAC ION HYDRATION: EXPERIMENTAL AND THEORETICAL SEARCH FOR ANION PAIRS

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Self-assembly of organic ions in aqueous solutions is a hot topic at the present time, and substances that are well soluble in water are usually studied [1,2,3]. In this work, aqueous solutions of sodium diclofenac are investigated, which, like most medicinal compounds, is poorly soluble in water. Classical MD modeling of an aqueous solution of diclofenac sodium showed an equilibrium between the hydrated anion and the hydrated dimer of the diclofenac anion. The assignment and interpretation of the bands in the UV, NIR, and IR spectra are based on DFT calculations in the discrete-continuum approximation. It has been shown that the combined use of spectroscopic methods in various frequency ranges with classical MD simulations and DFT calculations provides valuable information on the association processes of medical compounds in aqueous solutions. Additionally, such a combined application of experimental and calculation methods allowed us to put forward a hypothesis about the mechanism of the effect of diclofenac sodium in high dilutions on a solution of diclofenac sodium [4].

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SOLID-LIQIUD PHASE EQUILIBRIA IN THE K^+, H^+ || Ox^{2-}, Cit^{3-} – H_2O SYSTEM AT 298.15 K

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Solid-liquid equilibrium of multicomponent salt systems and its subsystem is necessary to describe phase formation in different industrial processes. Systems containing citrate find their application in medicine, food industry, desulphurisation process [1]; oxalate processes have great potential for the development of environmental methods for the extraction and separation of metals [2]. In this work, attention will be paid to K^+, H^+|| Ox^{2-}, Cit^{3-} – H_2O system, for which no information on liquid–solid phase equilibria has been found in the literature. Date on the thermodynamic properties and liquid-solid phase equilibria of smaller-dimensional systems: citric acid – potassium citrate – water [3] and oxalic acid – potassium oxalate – water [4] and their binary subsystems have been found in the literature at different temperatures.

The goal of the work is to obtain a set of experimental data on phase equilibria in the system, formed by oxalates and citrates potassium at 298.15 K, necessary for the further construction of thermodynamic models of reciprocal citrate-oxalate systems.

Phase equilibria in the reciprocal citrate oxalate system were investigated at 298.15 K by isothermal dissolution method. During the work, several methods were used to prepare the initial heterogeneous mixtures: from oxalic and citric acids, potassium hydroxide and water, from pre-synthesized salts – oxalate and citrate potassium, and by slow evaporation of water from the solution until a heterogeneous mixture was formed.

The resulting phases under given conditions – the solution and precipitate, separated by vacuum filtration method were analyse. The phase composition of the precipitates was determined by X-ray phase analysis (XRD). The concentrations of citrate and oxalate ions in saturated solutions above the precipitate were determined by ion chromatography and concentration of acids by potentiometric titration methods.

The influence of various factors on the conditions of crystallization of solutions of the system under study was tested: holding time of the initial mixtures, presence of a seed, stirring.

Isothermal cross section of phase diagram of the K^+, H^+ || Ox^{2-}, Cit^{3-} – H_2O system was constructed at 298.15 K by experimental data, received in work. It has been established that in the system K^+, H^+ || Ox^{2-}, Cit^{3-} – H_2O the time to reach equilibrium is significantly influenced by the mixing of the initial mixtures and the study of this reciprocal system is complicated by the presence of metastable equilibria that are stable over a long period of time.

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THE EFFECT OF STRUCTURAL AND SOLVATION FACTORS ON SPECTRAL CHARACTERISTICS, STABILITY, AFFINITY TO BIOSTRUCTURES OF *α*-BODIPY CARBOXYLIC ACID AND ITS CONJUGATES WITH MONOTERPENOIDS

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The antibiotic resistance is one of the most significant problems in the modern world. The growth rate of the variety of pathogenic strains resistant to known antibiotics exceeds the number of developed drugs. This situation led to the search or new types of compounds – theranostics. The being used of these allows for the simultaneous diagnosis and treatment of various types of diseases. The particular interest among the newly obtained compounds are BODIPY conjugates with membranotropic monoterpenoids. When introduced into living organisms, these compounds can perform at least two functions: fluorescent intracellular imaging and elimination of infectious pathogens without the development of resistance.

The report will present the results of a comparative analysis of the influence of the molecular structure features and the nature of the medium on the spectral characteristics, photo- and pH stability, as well as affinity to biostructures of the first obtained conjugates of α-BODIPY carboxylic acid **1** with myrtenol and thioterpenoid **2** and **3** respectively (Figure 1).

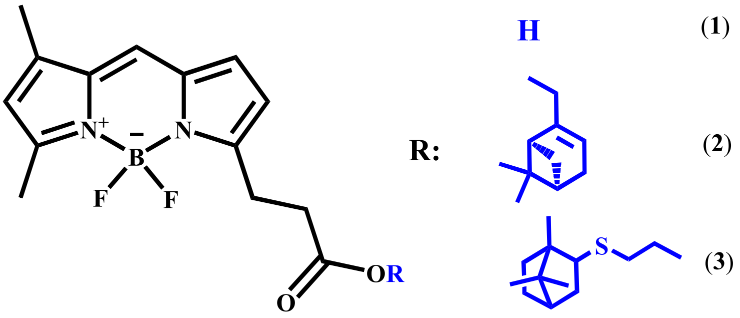

Figure 1. Molecular structures of *α*-BODIPY-propanoic acid **1** and their terpene-BODIPY conjugates **2** и **3**.

Both conjugates are sufficiently photostable ($t_{1/2}$ ~5–40 ч) and exhibit high fluorescence efficiency (φ ~75–90%) in naturally nonpolar and polar electron- or proton-donating solvents (cyclohexane, toluene, 1-octanol, 1-propanol, ethanol, DMF, DMSO). The advantage of conjugates **2** and **3** is their lack of sensitivity of fluorescence to the acidity of the medium. This is confirmed by the results of studies conducted in aqueous ethanol media with a pH ranging from 1.65 to 9.18. In such solutions, the stability of luminophores is maintained for a long time (more than a week), increasing their practical potential. It has been shown that the affinity for lipid structures in conjugates **2** and **3** is significantly higher than in the initial acid **1**. At the same time, the conjugate with thioterpenoid (**3**) exhibits pronounced antimycotic activity against yeast fungi.

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BODIPY CARBOXYLIC ACIDS AND THEIR ETHERS AS FLUORESCENT MARKERS FOR BIOIMAGING

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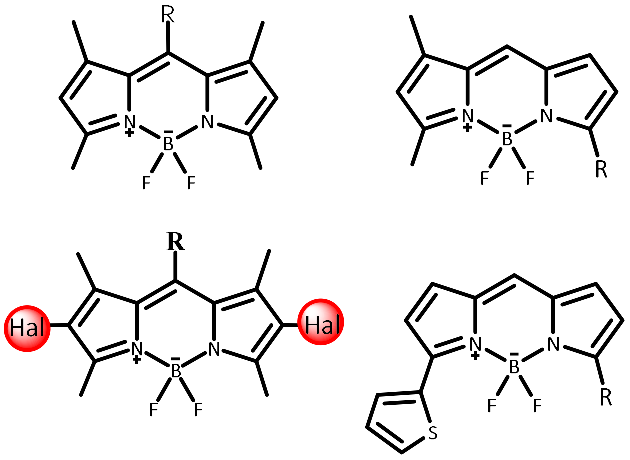
BODIPY dyes are a well-known class of compounds that have excellent photophysical properties, making them popular for a wide range of biological and medical applications. Low-molecular, low-polarity boron(III)dipyrromethates are able to easily penetrate the cell membrane and specifically stain cell organelles. Therefore, at present, one of the current directions is the development of effective fluorophores based on BODIPY and their use for bioimaging, the methods of which are widely practiced in preclinical experimental studies (monitoring the delivery of drugs to cancer cells, studying the dynamics of accumulation and localization of a fluorescent agent).



R: $-(CH_2)_nCOOH$
$-(CH_2)_nCOOCH_3$
$n = 2, 3, 4$
Hal: **I, Br**

The report will present the results of a comparative analysis of the influence of the molecular structure features and of the medium nature on the spectral properties, photo-, pH stability and affinity to biostructures of alkyl and halogen-substituted BODIPY dyes containing carboxylic acid residues and their esters at the *α*- and *meso*-positions of the dipyrromethene core.

It has been established that all the studied compounds are pH stable and retain fairly intense fluorescence in solvents of the various natures, including acidic and alkaline media (up to φ ~40–90%), which is a practically significant criterion for fluorescent biomarkers. The fluorescence quantum yield noticeably decreases (from 50 to 2%) for diiodine- and dibromo-substituted BODIPYs, while high values of the singlet oxygen generation quantum yield are recorded (up to $\Phi\Delta$ ~80%), which provides enormous potential for the practical use of the halogen-substituted dyes as effective photosensitizers. It was found that, regardless of the medium properties, the replacement of the hydrogen atom in the BODIPY *meso*-spacer by bulky aliphatic substituents contributes to the stabilization of the fluorophores by almost ~2–3 times compared to *meso*-unsubstituted analogues. The observed effect may be due to manifestation of the effect of steric screening of the *meso*-methine group bonds as the most chemically active fragment of the conjugated BODIPY system of the fluorophores.

The spectral and biological studies carried out allowed us to conclude that the halogenation and conjugation of BODIPY carboxylic acids with biomolecules, including drug monoterpenoids, makes it possible to obtain promising multifunctional dyes that are in demand for fluorescent diagnostics and photodynamic inactivation of pathogenic microorganisms.

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LABILE STATES ARE THE BASIS OF FUNCTIONAL MATERIALS

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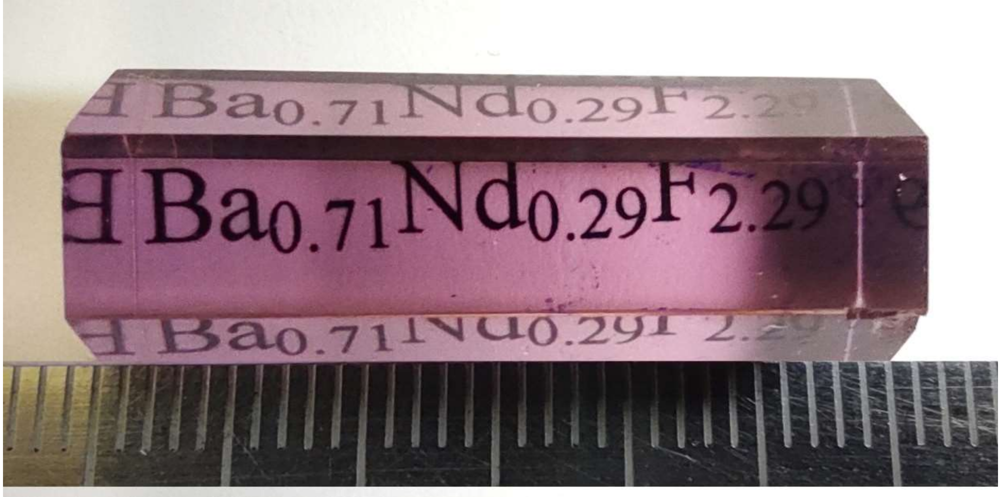
The available data refute the well-known postulate of thermodynamics, namely, it is generally accepted that labile states are unrealizable, because its transition to the equilibrium state is not associated with overcoming the potential barrier, there is no force that returns the system to its original state, and after the fluctuation out of equilibrium, the system moves away from it with acceleration [1-3].

There are well-known situations when the system exits the labile state extremely slowly. The corresponding states are not only observable, but also make it possible to create durable functional materials. A striking example is solid solutions that are thermodynamically unstable at low temperatures, but show no signs of spinodal decomposition. For example, the crystalline solid solution $Ba_{1-x}Ca_xF_2$ samples, prepared by mechanochemical treatment, can exist in a non-equilibrium state indefinitely. After heating, the system goes to the equilibrium state, namely, the decomposition of the solid solution takes place, and it is accompanied by heat release (exothermic effect) [4]. Apparently, the relative stability of the crystalline samples of the $Ba_{1-x}Ca_xF_2$ solid solution is due to the extremely low values for the diffusion coefficients of the cations. The system is “falling”, but very slowly.

Frozen labile states with the architecture of spinodal decomposition in the initial stage can be optically transparent single crystals - photonics materials.



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LOW-TEMPERATURE HEAT CAPACITY OF CADMIUM TUNGSTATE

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Cadmium tungstate belongs to the family of metal molybdates and tungstates, which are the subject of extensive research due to their unique optical properties, which determine a number of practical applications. For example, $CdWO_4$ is used as a Raman laser material [1,2], as a detector in spectrometric and radiometric devices, including X-ray computed tomography [3]. Also, $CdWO_4$ is a promising bolometric detector material for rare event searches, especially for the search for neutrinoless double beta decay [4,5]. Currently, many properties of cadmium tungstate have been investigated, including its structure [6], thermal conductivity [7], melting point of 1598 K [8], but there is no information on its heat capacity.

A $CdWO_4$ single crystal was grown by the original low-thermal-gradient Czochralski technique [9]. Then, the single crystal samples of the required shape and size were made from it to investigate its properties. The heat capacity of cadmium tungstate was measured by the relaxation method in the temperature range of 2.4–221.7 K on the PPMS-9+Evercool II system (Quantum Design, USA) at the Resource Center of the SPbU Research Park. At higher temperatures from 79.4 to 310.9 K, the heat capacity was measured on the unique hand-made adiabatic calorimeter [10] at NIIC SB RAS. In the range of 79.4–221.7 K there is a coincidence of experimental data within the uncertainty of their measurement. No anomalous behavior of heat capacity associated with the presence of any phase transitions was found.

The Debye T^3 law is a widely used method for extrapolating experimental data to zero temperature. In this case, it was applied based on six experimental points below 4 K.

Extrapolation of the experimental data to zero temperature was performed using the Debye T^3 law, based on six experimental points below 4 K. The smoothed heat capacity function in the range of 0–311 K was obtained using the unified equation (see [11,12]), which is a combination of the Debye model and the superposition of Einstein models.

Using the provided data, we calculated the thermodynamic functions of cadmium tungstate, including entropy, enthalpy increment, and Gibbs free energy. Additionally, we calculated the characteristic Debye temperature at zero.

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LOW-TEMPERATURE HEAT CAPACITY OF ZINC TUNGSTATE

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Zinc tungstate, $ZnWO_4$, is a promising cryogenic bolometer, laser material and scintillator [1-5]. The structure of $ZnWO_4$ has been studied [6], the melting point is 1473 K [7]. Experimental data on heat capacity in the range of 5–550 K [8,9] and 81–301 K [10], as well as enthalpy increment at high temperatures up to 1200 K [11], are available in the literature. The literature data show atypical behavior near zero and are not consistent with each other.

The single crystal used in the study was grown by the low thermal gradient Czochralski technique. To clarify the values of heat capacity at near-zero temperatures, an experimental study of the heat capacity of a zinc tungstate single-crystal sample in the 2.6–220 K range was carried out using the relaxation method. Based on the experimental data, a physically reasonable equation was used to describe experimental heat capacity of $ZnWO_4$ in the low-temperature range. No anomalous behavior of heat capacity associated with phase transitions was found.

Note that the work [9] is the work [8] with revised experimental data, so the comparison will be made only with data [9]. Comparison with known data showed that the experimental heat capacity [9] systematically deviates from both the heat capacity obtained by us and the one given in [10]. For example, the value of heat capacity we obtained at standard temperature coincides with the value in [10] within the experimental uncertainty and is 4.5% lower than the value indicated in [9]. Furthermore, in the very low temperature range, the heat capacity in [9] displays an anomalous contribution, which is apparent in the C/T^3 coordinates or in calculating the temperature dependence of the Debye temperature. For example, the heat capacity of ZnO has an anomalous component in the low temperature region associated with the Schottky effect [12], the contribution of which can give the detected effect of atypical behavior of the heat capacity [9] near zero. These facts suggest the presence in the heat capacity of the sample [9] of a contribution related to impurity phases. This may be zinc oxide, the impurity of which at the level of a few percent may not have been detected on the analytical equipment of that time.

Using both the present work data and data [10], we obtained a smoothed description of the heat capacity of $ZnWO_4$ in the range of 0–301 K. Based on these results, we were able to calculate the thermodynamic functions of zinc tungstate, including entropy, enthalpy increase, and Gibbs free energy. The characteristic Debye temperature at zero was also calculated.

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METHODS OF DEFINING THE DECOMPOSITION TEMPERATURE OF RUTHENIUM TRICHLORIDE DISSOLVED IN LICL-KCL-CSCL MELT

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The behavior of ruthenium directly depends on the stability of complex compounds of ruthenium ions in the melt. Ruthenium trichloride exists in the LiCl-KCl-CsCl melt in the form of thermally unstable complex ions $[RuCl_6]^{3-}$. Analysis of literature data shows that the decomposition temperature of the complex ion $[RuCl_6]^{3-}$ has not been studied in any chloride melt.

Reference temperature points were chosen with an interval of 10 °C because of the errors created by an induction furnace. For greater accuracy determination of the decomposition temperature was carried out by four methods, each of which has its own advantages and disadvantages, and it is impossible to single out any one.

Electrochemical method involves observing the change in electrode potential by the EMF method over time. An electrochemical cell was constructed using a two-electrode scheme.

Electronic absorption spectroscopy involves measuring the optical density of electronic absorption spectra over time. A point on all compared spectra corresponding to the same wavelength (preferably the point of maximum or close to it) was chosen to plot the curves of concentration vs time. The spectra are pre-aligned at zero optical density in the long-wavelength region.

The visual method was also used in parallel with the spectroelectrochemical method. The colour of the melt during the measurements and the salt before/after the experiment are observed, and the presence/absence of metallic ruthenium precipitate is recorded.

The experimentally obtained values agree very well with the theoretical values calculated semi-empirically on the basis of the equation of the conditional standard Gibbs energy of formation of a dilute solution of ruthenium trichloride from simple elements in the molten eutectic mixture LiC1-KC1-CsC1. This equation was derived from the thermodynamic dependence of the conditional standard potential, which in turn was determined from the experimentally obtained values of the equilibrium potential of the Ru^{3+}/Ru redox pair.

Thus, the use of several methods simultaneously to analyze experimental data has many advantages: high reliability of the obtained results and high accuracy of the calculated data, reproducibility. The use and combination of the described research methods allows to obtain reliable and complete thermodynamic information about the process under study.

NON-COVALENT INTERACTIONS OF DRUGS WITH BIORELEVANT MEDIA COMPONENTS

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Dissolution process is a key step in the uptake of oral drugs since the bioavailability and therapeutic effect are mainly determined by solubility and dissolution rate of an active pharmaceutical ingredient. A number of approaches including employment of solubilizers and drug delivery systems are known and used to improve these parameters. Nevertheless, the solubility and dissolution rate are affected not only by the solubilizers, but also by the composition and pH of the medium. The complexity of biological fluids, where the dissolution of orally administrated drugs takes place, represents a significant challenge to understanding the drug behaviour.

Generally, water or buffers are commonly used as dissolution media in experiments *in vitro*. However, this may lead to false impressions because these media are quite different from biological fluids *in vivo*. Components of body fluids can interact with drugs and change their pharmacologically important properties. In this connection, biorelevant media were devised to compositionally mimic the physiological fluids and to predict the processes *in vivo*.

In this work, the influence of biorelevant madia FaSSGF (Fasted State Simulated Gastric Fluid, pH 1.6) and FaSSIF (Fasted State Simulated Intestinal Fluid, pH 6.5) on solubility and dissolution rate of drugs was studied. The obtained results are discussed in terms of possible interactions of drugs with sodium taurocholate, which is the main component of biorelevant media and capable to aggregation in aqueous solutions. The influence of structure and ionization state of drugs on the interactions with taurocholate is analysed. The selectivity of binding of the drugs with the unimers and aggregates of taurocholate is discussed.

METAL β-DIKETONATES AS PRECURSORS IN MOCVD PROCESSES: THE THERMODYNAMICS OF THEIR EVAPORATION

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Volatile metal β-diketonates are widely used as precursors for the preparation of various functional coatings by MOCVD. The first step of this process is the evaporation of the precursor(s), therefore, to select precise deposition conditions, it is necessary to have reliable knowledge of their vapor pressure and thermodynamic characteristics of sublimation or vaporization (enthalpy and entropy), which vary significantly depending on the combination of the central atom and ligand environment. Moreover, the data available in the literature tend to have a significant scatter [1].

With the purpose of obtaining reliable thermodynamic data, we began to develop a technique for diagnosing the quality of thermodynamic data, the essence of which is to establish the relationship between the composition and the corresponding properties in the series of various metals with β-diketonates. The necessary condition for its realization is the presence of a base series of metal β-diketonates with reliable thermodynamic data.

In this work, we applied a diagnostic technique to check the quality of the limited set of available data on Ir(III) complexes with β-diketones [2]. For this purpose, scandium(III) β-diketonates, whose thermodynamic characteristics were verified earlier, were used as a base series [1]. The thermodynamic characteristics were standardized using the developed methodology. The implemented approach requires the presence of a molecule, well characterized in thermodynamic terms, which can be assigned as a "base" – for *tris*-complexes, these are often metal acetylacetonates [3]. To fulfill this condition, we verified both the literature and our data on the melting, sublimation and vaporization processes of *tris*-acetylacetonates of Al, Sc, Cr, Mn, Fe, Co, Ru, Rh, In, and Ir.

The approach can be transferred to metal complexes with other oxidation numbers (+1, +2, +4), including heteroligand compounds.

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COMPREHENSIVE THERMODYNAMIC STUDY OF 1-*TERT*-BUTYL-3-NITRO-1*H*-1,2,4-TRIAZOLE IN THE RANGE OF (0–T_m) K

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A comprehensive experimental and theoretical study of the thermodynamic properties of the 1-*tert*-butyl-3-nitro-1*H*-1,2,4-triazole ($C_6H_{10}N_4O_2$, CASRN 1185760-32-0) was carried out. The heat capacity of the substance under vapor saturation pressure $C_{s,m}$ in the temperature range of (8 to 370) K was determined using a Termis TAU-10 automatic vacuum adiabatic calorimeter [1]. Obtained experimental temperature dependance of heat capacity was used to calculate standard thermodynamic functions of the compound, including the absolute entropy ($S°$), in temperature range of (0 – T_m) K (Figure 1).

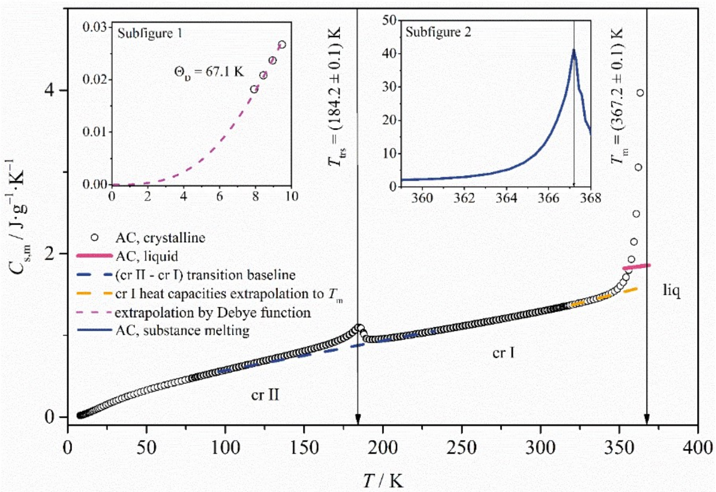

Figure 1 – Temperature dependance of the 1-*tert*-butyl-3-nitro-1*H*-1,2,4-triazole heat capacity in the range of (0 – 370) K

Saturated vapor pressure p_{sat} for crystalline compound in the interval of (303 to 333) K was measured using the integral Knudsen effusion method [2] and in the interval of (304 – 361) K using the Mettler Toledo Flash DSC1 [3]. The energy of combustion $\Delta_c U°$(298.15 K) of the crystal was measured in a series of experiments in a modified combustion calorimeter B-08-MA with a static bomb [1]. Ideal-gas thermodynamic properties of 1-*tert*-butyl-3-nitro-1*H*-1,2,4-triazole were calculated by statistical thermodynamics using the "rigid rotor – harmonic oscillator" approximation with the correction to the internal rotations, available in the molecule, using the "1-dimensional hindered rotor" formalism. Standard formation enthalpy $\Delta_f H°$(298.15 K) of the ideal-gas 1-*tert*-butyl-3-nitro-1*H*-1,2,4-triazole was calculated in the framework of the isodesmic and homodesmotic reactions approach. Experimental and theoretically calculated entropy and enthalpy of formation of a compound in the ideal gas state are in good agreement.

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THE INFLUENCE OF THE MOLECULAR STRUCTURE OF BODIPY ON THEIR AFFINITY FOR BLOOD TRANSPORT PROTEINS

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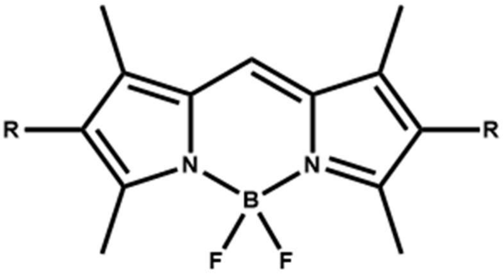
Boron(III)dipyrromethanates constitute a relatively new class of fluorophores that have garnered significant attention from scientists in recent years. These dyes offer notable advantages, including their spectral and luminescent properties (such as high quantum yields and molar absorption coefficient values), as well as their thermal and chemical stability. Additionally, the hydrophobic nature of most compounds in this class allows for their utilization as probes for various biological entities, such as proteins. Serum albumins serve as the primary transport proteins in the blood. While bovine serum albumin (BSA) is often utilized in research due to its structural similarity to human serum albumin (HSA), it is crucial to note that despite their structural similarities, these proteins may exhibit distinct ligand-binding behaviors. Therefore, it is important to study systems involving both proteins to elucidate and highlight the differences in the processes of supramolecular complex formation between serum albumins and small ligands.



R: H (1), CH_3 (2), C_2H_5 (3), C_3H_7 (4), C_4H_9 (5)

Figure 1. BODIPY 1-5 structures

The objective of this study was to investigate the processes of supramolecular complex formation between 2,6-alkyl-substituted BODIPY and serum albumins (Figure 1). In the initial phase of our research, we carried out modeling of BODIPY-protein systems by means of molecular docking approaches. Subsequently, we investigated BODIPY-protein isomolar series (with constant BODIPY concentration) in a PBS-DMSO medium employing various spectral methods. The experimental results revealed that all BODIPYs form stable supramolecular complexes with albumins, and systems exhibiting fluorescence quenching (BODIPY 1, 2) were analyzed using the Stern-Volmer theory. Thermodynamic parameters were also determined for these systems. In contrast, for other systems (BODIPY 3 - 5), an increase in fluorescence was observed, likely due to the disaggregation of BODIPY within the hydrophobic protein pocket. Furthermore, Förster resonance energy transfer (FRET) parameters were determined for all systems, with the energy transfer efficiency increasing from BODIPY 1 to BODIPY 5 for both proteins, aligning well with computational predictions. For BODIPY 1, the detection limits of serum albumin were determined, and selectivity was assessed in the presence of both proteins in solution.

The findings of this study underscore the significance of further investigating dyes in conjunction with transport proteins. Moreover, the potential application of the studied dyes in clinical medicine for the early diagnosis of kidney diseases or in biochemistry for addressing proteomics challenges is highly promising.

CAN WE CALCULATE WITH EXPERIMENTAL ACCURACY VOLUMETRIC THERMODYNAMIC PROPERTIES FOR AQUEOUS SOLUTIONS OF NONELECTROLYTES USING MOLECULAR DYNAMICS?

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Currently, molecular dynamics is actively used to solve a variety of scientific and practical problems, while the requirements for the accuracy of the results obtained are also in a very wide range. In some cases, differences between calculated and experimental values of 3–5%, and sometimes 10–20%, can be considered as an excellent agreement if, for example, the uncertainty of the experimental values is within approximately the same range, or if such deviations do not have a significant impact on the simulated processes, etc.

At the same time, for many aqueous solutions in certain concentration and temperature ranges, rather weakly expressed effects are observed experimentally, but their occurrence is associated with a change in the structure of liquids, which can be meaningful, for example, for biochemical processes. Accuracy of instruments used to measure density, compressibility, heat capacity, etc. for scientific purposes, allows these effects to be reliably detected, but can they be revealed based on the results of molecular dynamics modeling?

To answer this question, the report will use both the author’s own data, obtained from modeling and experimental studies of aqueous solutions, and those available in the literature. The main attention will be paid to binary systems in the temperature range from 283 to 313 K and with low to medium content of non-aqueous components, since it is under these conditions some peculiarities of thermodynamic properties are most often observed. Systems with non-aqueous components of different chemical natures (aliphatic alcohols, diols, amides, ketones, nitriles) will be compared. When presenting molecular dynamics calculations for each property under consideration, the degree of influence on the final results such factors as the number of atoms in the model box in simulations with periodic boundary conditions, the length of the trajectory after reaching equilibrium, the averaging procedure, the calculation methodology (in cases of reasonable alternatives) will be discussed.

THERMODYNAMIC AND MAGNETIC PROPERTIES OF YTTERBIUM TRIFLUORIDE AT LOW TEMPERATURES

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Fluorides of rare earth elements are widely used in precision metallurgy, laser technology, optics and other fields of technology. At the same time, many properties of these compounds, including thermodynamic and magnetic at low temperatures, have not been sufficiently studied.

One of the main features of the thermodynamic and magnetic properties of the compounds under study is the strong influence of the crystal field on them. The crystal field is created by the environment of the rare earth ion and depends on the interatomic distances and the symmetry of this environment, i.e. on the structural features of the crystal. The action of a crystal field leads to the emergence of a system of Stark levels, the population of which determines many physical properties (in particular, heat capacity, magnetic susceptibility) of crystals. Thermal population of Stark levels, which arise when the crystal field splits the main term of a rare-earth ion, leads to an additional contribution to the heat capacity (and, accordingly, to entropy and other thermodynamic functions). This additional contribution is called the Schottky anomaly. In this work, the splitting spectrum of the main term of the Yb^{3+} ion in the crystal field of ytterbium trifluoride was determined based on a study of heat capacity and magnetic susceptibility.

A sample of ytterbium trifluoride, YbF_3, was prepared and purified by Sigma-Aldrich. The purity of the commercial sample was better than 99.98%. No additional sample purification was used. Before conducting the research, the sample was characterized by X-ray phase analysis (Shimadzu XRD-7000 diffractometer), X-ray fluorescence analysis (Bruker M1 Mistral spectrometer), and inductively coupled plasma atomic emission spectrometry (VMK-Optoelectronics Grand-ISP spectrometer).

The heat capacity of the sample was measured using a vacuum adiabatic calorimeter (laboratory made) [1] in the range of 5 – 300 K. The calorimetric ampoule was a copper cylinder coated with silver, with a volume of 6 cm^3. Temperature was measured using germanium and platinum resistance thermometers. The experimental heat capacity was used to calculate integral thermodynamic functions in the range 0 – 300 K.

The magnetic properties of the polycrystalline sample were studied using a SQUID magnetometer (MPMS-XL Quantum Design) in the temperature range 1.8 – 300 K in a magnetic field $H = 1$ kOe. At room temperature, the measured effective moment corresponds to that expected for Yb^{3+} ions, which have a total moment of 7/2, composed of spin 1/2 and orbital momentum 3.

The Schottky anomaly was isolated from experimental heat capacity data using Westrum's scheme [2]. For this purpose, we additionally used literature data on the heat capacity for GdF_3 and LuF_3. The anomalous entropy values made it possible to determine the multiplicity of the lowest Stark component. The multiplicity of degeneracy of other Stark levels, as well as their energies, were determined as a result of a joint analysis of the anomalous heat capacity and the paramagnetic component of magnetic susceptibility.

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DYNAMIC SURFACE ELASTICITY OF DISPERSIONS OF BOVINE SERUM ALBUMIN FIBRILS

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Many proteins and their aggregates have a high surface activity and can be used to stabilize dispersion systems in pharmaceutical and food industries, where the use of inorganic stabilizers is very limited. At the same time, while high concentrations of native proteins are often required for these purposes, the application of fibrils reduces the total protein concentration, and thereby decreases the cost of the products. Bovine serum albumin (BSA) is a typical globular protein, which can form fibrils in vivo and in vitro. Despite the high surface activity of BSA fibrils in aqueous solutions, so far the main attention has been paid only to the methods of synthesis, morphology and volume properties of these systems. As far as we know, the surface properties of aqueous dispersions of BSA fibrils have not been studied yet.

Curly worm-like fibrils of BSA were obtained in this work. These fibrils differ significantly in shape and size from the previously studied fibrils of other globular proteins [1]. Methods of surface rheology were used to study the mechanism of the adsorption layer formation of BSA fibrils on the water surface. Atomic force microscopy and Brewster angle microscopy were used to determine the micro and mesoscopic morphology of these layers. Bovine serum albumin fibrils form continuous layers on the water surface, which do not collapse when the surface is strongly compressed. At the same time, these layers become rigid after strong compression and are characterized by relatively high values of the surface pressure and surface elasticity as compared to native protein layers. The adsorption layers of BSA fibrils differ from the layers of native protein also by the appearance of an induction period in the kinetic dependencies of the surface properties, the duration of which increases when the dispersion of fibrils is purified from surfactants formed during their synthesis. An increase in the ionic strength of the solution significantly slows down the change of surface properties of the dispersions of BSA fibrils, similar to the dispersions of lysozyme fibrils [1], which indicates a strong influence of electrostatic interactions in the layers of BSA fibrils. The properties of the spread layers of BSA fibrils differ from the properties of their adsorption layers. This difference may be caused by the slow propagation of fibrils along the interface after their spreading to the water surface and/or a lower concentration of surfactants that remain in the dispersion even after cleaning, in the case of spread layers.

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STUDY OF SUPRAMOLECULAR COMPLEXES FORMED BY BODIPYS AND SERUM ALBUMINS

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In recent years, a relatively new class of fluorescent dyes, boron(III)dipyrromethenates or BODIPYs, has garnered attention. The relative simplicity of their structural modification makes it possible to tune many photophysical properties, such as molar absorption coefficient and fluorescence quantum yield. Most BODIPYs possess hydrophobic properties, allowing them to be utilized for marking and visualizing various biological structures with hydrophobic regions. This study investigates the processes of supramolecular complex formation involving three BODIPY-based compounds with bovine and human serum albumins (BSA and HSA), which are the primary blood transport proteins.

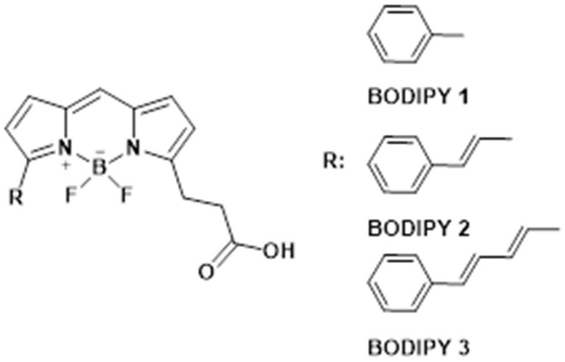

Figure 1. BODIPY 1-3 structures.

Prior to the commencement of the study, computer modeling of BODIPY-protein systems was carried out using the molecular docking method. The simulations were performed using AutoDock 4.2 software, establishing parameters and binding sites for BODIPY 1-3 with the proteins. The resulting binding energy values indicate a high affinity of these dyes to albumins. The experimental phase of the study utilized the isomolar series method in a phosphate buffer (pH = 7.42). The observed BODIPYs fluorescence quenching in the presence of serum albumins is explained within the Stern-Volmer theory. Time-resolved fluorescence spectroscopy results corroborated the conclusions regarding the fluorescence quenching mechanism. It was determined that BODIPY-protein complexes exhibit a mixed mechanism, with a prevalence of the dynamic mechanism in BODIPY-BSA complexes and the static mechanism in BODIPY-HSA complexes. Thermodynamic parameters were determined using the Scatchard and Van't Hoff equations, which align with the results of computer modeling. In all investigated systems, the FRET energy transfer mechanism was identified, and its parameters and efficiency were determined.

These findings suggest the potential utility of BODIPY 1-3 as fluorescent markers in biological systems, applicable in biochemistry for proteomics tasks or in clinical medicine for the early diagnosis of kidney disorders.

PROPERTIES OF SPREAD LAYERS OF PLANT PROTEIN AGGREGATES

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Proteins and their aggregates provide important functions in biological systems and are used industrially to stabilize foams and emulsions. Amorphous protein aggregates (microgels) can be more effective stabilizers compared to native proteins [1]. However, information on the thermodynamic characteristics of adsorption and spread layers of protein aggregates is extremely limited at present, especially in the case of layers of plant protein aggregates.

Cupin-1.1 represents the domain of vicilin, a pea storage protein, and was obtained using a previously created plasmid vector and *E. coli* strain BL21 [2]. In this work, spread layers of amorphous aggregates of cupin-1.1 at the air/water interface were studied using surface tensiometry, dilatational surface rheology, and atomic force microscopy.

As the surface pressure increases, the dynamic elasticity of the layer passes through two local maxima, and the elasticity value in the region of the second maximum is four times higher than the value in the region of the first maximum. At the beginning of compression, the soft corona of microgel particles is stretched along the surface, and during compression, interaction occurs between the coronas of particles, which leads to an increase in surface elasticity. With further compression, loops and tails are formed that penetrate into the substrate, which leads to a surface elasticity decrease [3]. Transmission electron microscope images of an aqueous dispersion of cupin-1.1 indeed indicate the presence of a corona on the surface of cupin-1.1 aggregates. A following increase in dynamic surface elasticity after a local minimum is probably caused by interactions between the hard cores of aggregates, which ultimately leads to the formation of multilayer structures at high surface pressures. In this case, the surface elasticity begins to decrease due to the exchange of segments between different layers at the interface [4].

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THERMODYNAMIC STUDY OF MULTICOMPONENT OXIDE SYSTEMS ON BASE OF CERIUM OXIDE BY KEMS METHOD

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The various CeO_2 based systems is of practical interest because their high ion conductivity and potential using for SOFC. Prediction of the behavior at high temperatures of such systems require the information of quantitative composition of vapor as well as thermodynamic properties (such as activities, activity coefficients and partial thermodynamic functions) for all components. In this study some ceria-containing systems were studied by Knudsen effusion mass spectrometry (KEMS). In particular the vaporization processes and thermodynamic properties of MO-CeO_2 (here and after M=Ca, Sr, Ba), CeO_2-ZrO_2, CeO_2-Y_2O_3 and CeO_2-Gd_2O_3 systems as well as thermodynamics of some gaseous cerium oxyacid salts was carried out (KEMS). Investigation was done using MS 1301 mass spectrometer at the ionization energy equaled to 30 eV. Vaporization of the samples under consideration was carried out from molybdenum and tungsten effusion cells heated by the electron bombardment. Temperature was measured by optical pyrometer EOP-66 with the accuracy ±10.

The CeO^+ and CeO_2^+ ions were detected in mass spectra above all studied systems in the temperature range 1950-2100 K. For CeO_2-Gd_2O_3 and MO-CeO_2 ions M^+, MO^+ and Gd^+, GdO^+ were also detected respectively. The mass spectrum analyses and appearance energies of ions in mass spectrum shown that the vapor over the systems consist of CeO, CeO_2 and O molecules. In some cases, second component is also present in the vapor phase in the given temperature range. The partial pressures of these vapor species were obtained using the ion current comparison method. For the MO-CeO_2 systems the standard formation enthalpies for $SrCeO_{3\ (s)}$ and $BaCeO_{3\ (s)}$ were determined. Additionally gaseous molecules $MCeO_3$ were detected in the vapor. For these species standard formation enthalpies were derived.

In all studied systems ceria is stabilized by second component and decomposition to Ce_2O_3 in the condensed phase wasn't observe. The activities of CeO_2 MO and Gd_2O_3 activities in the MO-CeO_2 and CeO_2-Gd_2O_3 systems at the temperature 2000 K were found by the differential mass spectrometric method using ceria, MO and Gd_2O_3 as the standard of the determination of the component activities. In the CeO_2-Gd_2O_3 the activities of components were also derived by Belthon – Fruehan method [1]. The ZrO_2 and Y_2O_3 activities in the samples studied were calculated according to the Gibbs-Duhem equation. All systems under study demonstrate low negative deviation from ideal case.

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The financial support of Russian science foundation (research project 24-23-00047). The authors are grateful to the Cryogenic department of the Science Park of St. Petersburg State University for the uninterrupted supply of liquid nitrogen. XRD studies were performed at Center for X-ray Diffraction Studies of St. Petersburg State University.

THERMODYNAMICS OF FORMATION OF METHOTREXATE INCLUSION COMPLEXES WITH MODIFIED β-CYCLODEXTRINS

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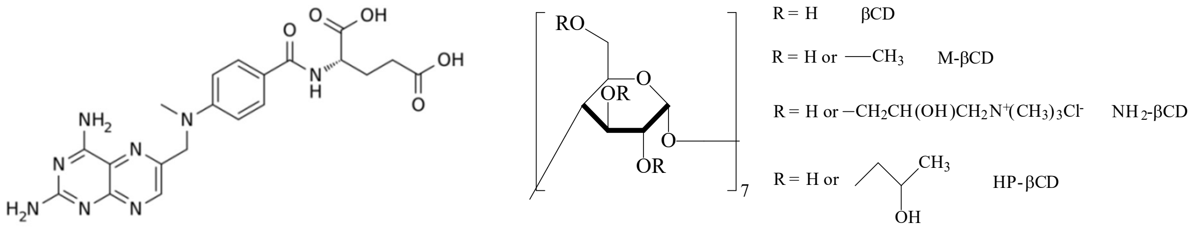
Significant number of insoluble drugs in the market provides the screening of appropriate approaches and methodologies to obtain the improved formulations providing faster dissolution and enhanced bioavailability active pharmaceutical ingredient. Methotrexate (MTX) is a drug widely used in the treatment of autoimmune and oncological diseases, however, its low solubility in aqueous media limits its application. β-Cyclodextrin (βCD), which is able to inclusion complex formation with MTX, can be used as safe and nontoxic solubilizer. However, βCD has limited solubility in aqueous media, which restricts its solubilizing activity. In this connection, modified β-cyclodextrins possessing higher aqueous solubility can be used as more effective solubilizers compared with the native βCD.



Structural formulas of MTX, βCD and its modified derivatives

In this work, complex formation of MTX with β-cyclodextrin, methyl-β-cyclodextrin (M-βCD), hydroxypropyl-β-cyclodextrin (HP-βCD) and amino-β-cyclodextrin (NH_2-βCD) with different ionized forms of MTX was studied using capillary electrophoresis, ^{1}H NMR and isothermal saturation methods. Effect of the nature of substituents surrounding the βCD cavity on the thermodynamics of complex formation and manifestation of the solubilizing effect is discussed. Based on a comparative analysis of ^{1}H NMR spectra, an assumption concerning the binding sites MTX with βCDs was made. The pH dependent complexation of βCDs with MTX is considered.

A NEW FULLY INSTRUMENTAL OPTICAL METHOD FOR DETERMINING CRITICAL PARAMETERS OF LIQUID MIXTURES

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A new fully instrumental optical method for determining the critical parameters of liquid mixtures is proposed, using two main universal features (criteria) of the liquid–gas critical point, namely, the achievement of an absolute maximum of light scattering intensity and the appearance/disappearance of a meniscus at the middle height of the optical cell. The method is implemented on a setup for measuring the intensity of Rayleigh light scattering with a horizontal scattering plane dividing the internal volume of the optical cell in half.

The essence of the method is to measure the temperature dependence of the intensity of light scattering by a mixture on a sequence of isochores crossing the vicinity of its critical point and to identify intensity anomalies of two physically different types, namely, well-known sharp (lambda-shaped) peaks of light scattering intensity associated with the transition of a near-critical mixture from single-phase into a two-phase state and narrow dips on their falling (low-temperature) branches associated with the passing of the meniscus from top to bottom through the horizontal scattering plane.

Based on the values of density, temperature and pressure corresponding to the indicated light scattering intensity anomalies, a boundary dew-bubble curve separating the regions of single-phase and two-phase states and a line of equal volumes of liquid and gas phases in the two-phase region are determined on the phase diagram of the mixture.

The peculiarity of the presented method for determining the critical parameters of liquid mixtures is that in a series of optical measurements (with one initial loading of the optical cell with a sample), the position of the critical point of the mixture on the experimentally determined boundary curve is determined by two physically different conditions imposed on opposite sides of the boundary curve. From the side of the single-phase region, the critical point of the mixture is defined as the point of the highest value of the measured light scattering intensity on the boundary curve. On the contrary, from the side of the two-phase region, the critical point is defined as the point where the line of equal volumes of the liquid and gas phases reaches the boundary curve.

The proximity or coincidence of two sets of values of critical parameters of liquid mixtures determined in this way clearly resolves the issue of the accuracy and reliability of their real experimental values. Presented optical method was tested on a number of model and reservoir hydrocarbon mixtures, previously studied by alternative experimental techniques.

The work was carried out within the framework of the Russian Fundamental Scientific Research Program, project No. 122022800364-6.

TRANSFORMATION MECHANISMS IN POWDER COMPRESSED TI-CUO UNDER CONTROLLED HEATING CONDITIONS

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The variety of studies on intermetallic systems illustrates much valuable information for understanding the mechanism of chemical reactions in such systems. To date, many studies have been published that have examined how different experimental conditions can affect the rate of chemical reactions. From the point of view of physical chemistry, a reaction cannot begin until the molecules in the reaction mixture overcome the energy barrier to reach the interatomic distance at which they can form a chemical bond, and from the point of view of thermodynamics, the occurrence of reactions is accompanied by an increase in entropy as a result mixing initial reagents and products. In the presence of a solid phase, mixing is difficult; therefore, the kinetics of such reactions is determined by both the internal reaction rate and mass transfer, which is necessary to replenish the amount of reagents that were consumed in the reaction zone. In this work, we study the process of phase formation in the Ti – CuO system during reaction sintering. In a simplified form, the transformation scheme can be presented as follows:

$$\mathrm{Ti+2CuO=TiO2+2Cu;}$$
$$\mathrm{xTi+yCu=TixCuy.}$$

The experiment is carried out at temperatures below the melting temperatures of the initial components, as well as at temperatures at which the liquid phase begins to appear. Before the experiment, the powders are ball-grinded, which increases the reactivity of the mixture. The results showed that the phase formation process begins long before the melting of the reactants, and aluminothermic reactions are the most exothermic. It is assumed that the metal particles are covered with an oxide film, the destruction of which lowers the energy barrier, as a result of which the first reaction occurs at a relatively high speed. A more complete reaction mechanism includes 8-10 stages.

To estimate the activation parameters and heats of reactions, data on which are absent in the literature, the model uses semi-empirical approaches. When formulating the thermokinetic model of reaction sintering, the classical Arrhenius law and the law of mass action are used. This model is implemented numerically.

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MOLECULAR DYNAMICS SIMULATION OF SELF-ASSEMBLY OF WATER REVERSE MICELLES WITH IMIDAZOLIUM IONIC LIQUIDS IN SUPERCRITICAL CARBON DIOXIDE

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Molecular dynamics (MD) simulations were used to investigate the self-assembly of water reverse micelles (RMs) with imidazolium ionic liquids (ILs) stabilized by dodecyl polyoxyethylene (3) polyoxypropylene (6) ether (LS-36) in supercritical carbon dioxide (scCO_2) at 308 K and 20 MPa. The study explored the impact of various factors, including the IL concentration, the alkyl chain length of the imidazolium cations (1-ethyl-3-methylimidazolium [EMIM]$^+$, 1-octyl-3-methylimidazolium [OMIM]$^+$), and the anion type (bis(trifluoromethylsulfonyl)imide [NTf$_2$]$^-$, tetrafluoroborate [BF$_4$]$^-$, acetate [ACE]$^-$) on the solubilization of ILs by water reverse micelles (Figure 1). The findings revealed that water, ILs, and the surfactant formed spherical RMs in the fluid phase, with varying structures depending on the hydrophobicity of the IL. The presence of ILs was found to expedite the self-assembly process and increase the number of assembled surfactants. Higher IL concentrations resulted in greater water content in the polar core of the RMs and reduced water solubility in scCO_2. The intermolecular interactions occurring between components of the systems as well as dynamical properties are discussed in terms of radial distribution functions, density distribution, hydrogen bond number and lifetime, number of contacts, and self-diffusion coefficients.

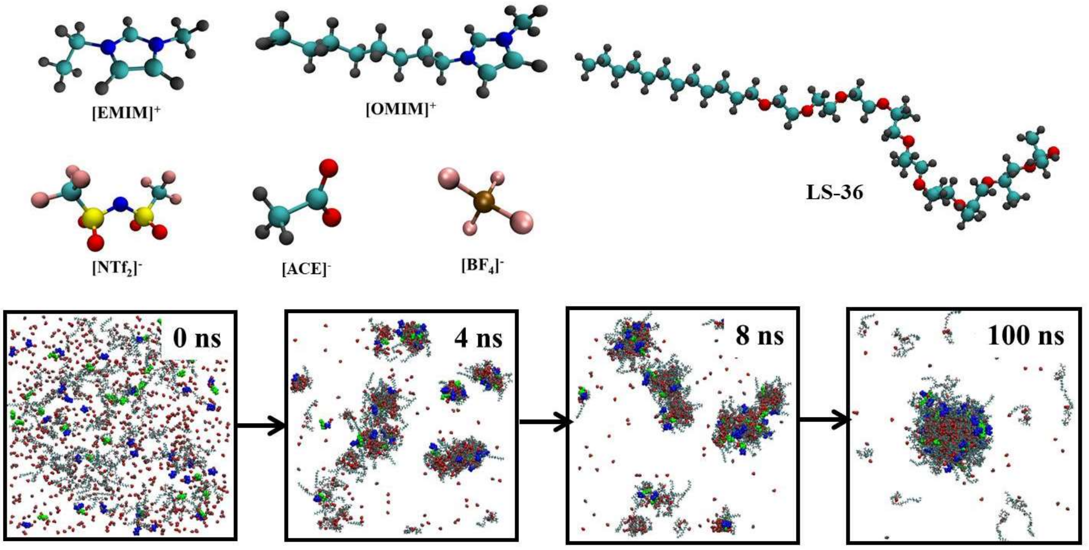

Figure 1. Schematic structure of cations ([EMIM]$^+$, [OMIM]$^+$), anions ([NTf$_2$]$^-$, [BF$_4$]$^-$, [ACE]$^-$), and dodecyl polyoxyethylene (3) polyoxypropylene (6) ether (LS-36) with designations of atoms. Symbols: nitrogen (blue), carbon (cyan), hydrogen (grey), boron (ochre), fluorine (pink), sulfur (yellow), oxygen (red). Time evolution of self-assembly process of water RM with [EMIM][NTf$_2$].

The calculations were performed on the supercomputer facilities provided by NRU HSE.

HALOGEN-FREE *BIS*(BODIPY) BICHROMOFORE PHOTOSENSITIZERS: INFLUENCE OF BODIPY UNITS LINKING POSITIONS ON SPECTRAL PROPERTIES AND AGGREGATION BEHAVIORS

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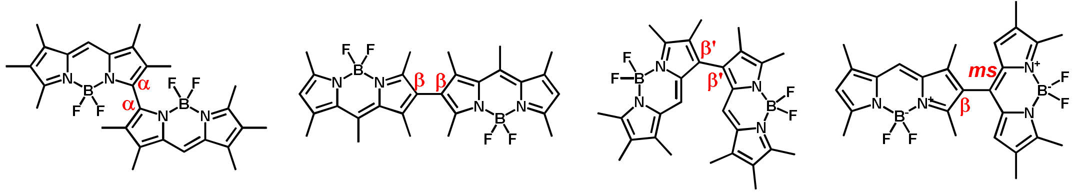
Currently, BODIPY compounds have been considered as effective biomarkers and photosensitizers (PSs) due to their good photostability, high molar absorption coefficients and fluorescence quantum yield and in some cases their ability to generate the reactive oxygen spices (RAS), including singlet oxygen. In addition, BODIPY compounds are easily undergo to structural modification in order to improve their significant properties.

Bis(BODIPY) PSs, consisting of two dipyrromethene units linked to each other, are being actively studied due to the absence of additional heavy halogen and metal atoms. The presence of additional halogens and heavy metals in the structure are undesirable due to potential harmful side effects. In this regard, *bis*(BODIPY)s are becoming increasingly promising for medical applications, in particular as fluorescent theranostics for diagnosis and treatment of diseases. Distinctive feature of *bis*(BODIPY) PSs is high fluorescence and phosphorescence sensitivity to the environment polarity, which is a desirable feature for activable PSs in photodynamic therapy of tumors. It is important to note that the spectral properties and singlet oxygen generation ability of *bis(*BODIPY)s significantly depend on the BODIPY units linking style.

In this report, we present synthesize and study the photophysical, photochemical and aggregation characteristics of *bis(*BODIPY)-based PSs with different linking positions of BODIPY units through the σ-bonds (Figure 1).



1 **2** **3** **4**

Figure 1. Objects of study

Compounds **1-4** are characterized by high molar absorption coefficients (ε), depending on the BODIPY domains linking positions of and the solvent polarity The highest ε values was observed for compound **2** (229087 and 181970 $l\cdot mol^{-1}\cdot cm^{-1}$ in benzene and DMF respectively). For **1-4** compounds, strong fluorescence quenching from Φ_{fl} = 0.91 to Φ_{fl} = 0.001 upon transition from non-polar (cyclohexane, benzene) to polar (DMF and DMSO) solvents is characterized. The highest quantum yield of $^1O_2$ generation ($\Delta\Phi$) was observed for compounds **1** and **4** in THF (0.90 and 0.88 respectively). The main disadvantages *bis(*BODIPY)s are their high hydrophobicity and inclination to aggregation in aqueous media, which leads to fluorescence quenching and loss of the ability to generate RAS. That's why, the report discusses the patterns of influence of the linking positions on their spectral aggregation behavior in THF-water mixtures.

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PLASMA-CHEMICAL SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF NANOSTRUCTURED MXENES OF COMPOSITION TiC_nCl_x

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In materials science, MXenes are a class of two-dimensional inorganic compounds that consist of atomically thin layers of transition metal carbides, nitrides or transition metal carbonitrides and have various hydrophilic groups [1]. A class of compounds such as MXenes was first reported in 2012, and their research has been is undergoing exponential growth, as evidenced by the number of publications where MXenest; is a keyword. Since 2020, the number of patents about MXenes has exceeded the number of journal articles, which proves that these substances are potentially commercially successful materials. The synthesized MXenes have an "accordion-like" morphology. MXenes may have on their surface functional groups, thus the general formula of MXenes is $M_{n+1}X_nT_x$, where T is a functional group (e.g., O, F, OH, Cl), M is a transition metal, X is an atom of carbon or nitrogen. Due to their structure, MXenes have unique electrical, magnetic, optical, biological properties. MXenes, as conductive layered materials with functional surface groups, have a wide range of promising applications as energy storage devices (lithium-ion batteries, supercapacitors). batteries, supercapacitors), materials for photocatalysis, as gas sensors, transparent conducting electrodes, electrochromic devices [2]. Production MXenes involves multi-step, extremely hazardous, environmentally harmful high-temperature processes of chemical etching of precursors, requiring further utilization of the reaction by-products. The precursors themselves have quite high cost. Any alternative methods of obtaining MXenes currently do not exist. The use of plasma discharges in contact with liquids, for synthesis of nanoparticles of metals and their oxides is considered in a number of review works [3]. But the absolute majority of studies have been carried out for discharges initiated in water, initiated in water. In this case, oxide nanoparticles are always formed. Discharge ignition in non-aqueous oxygen-free solvent (for example, tetrachloromethane) will allow obtaining metal carbide nanoparticles. In this work for the first time plasma-chemical synthesis of nanoparticles of MXenes type was carried out TiC_nCl_x composition by initiating a discharge between two titanium rods, immersed in tetrachloromethane. Tetrachloromethane was chosen as the oxygen-free solvent that has a relatively high boiling point and low dielectricity. boiling point and low dielectric constant. The electrophysical characteristics of the discharge were determined, the morphology of the formed particles was investigated, and their photothermal properties were studied.

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THERMOCHEMISTRY OF SOLVATATION AND VAPORIZATION OF MOLECULAR AND IONIC LIQUIDS

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The enthalpy of vaporization/sublimation is a crucial parameter for analyzing intermolecular interactions, solubility, and the volatility of pollutants [1]. However, experimental determination of this enthalpy can be challenging due to factors like high reactivity and difficulties in obtaining pure compounds. To address these challenges, empirical calculation methods based on the "structure-property" relationship have been developed, enabling the estimation of vaporization/sublimation enthalpies using structural parameters at a lower cost. Over the years, numerous additive calculation procedures have been proposed.

This study focuses on the limitations of a specific enthalpy calculation scheme, particularly regarding the varying impact of methylene groups on vaporization enthalpies across different homologous series. Interestingly, the contribution of methylene groups to solvation enthalpies remains consistent across homologous series. By exploring these discrepancies, we uncover patterns that not only apply to molecular liquids but also extend to ionic liquids.

Our research leads to the development of a method for determining vaporization enthalpies of both molecular and ionic liquids at 298.15 K. Furthermore, utilizing these identified patterns allows us to predict the dissolution heats of alkanes in both types of liquids. Comparison of the enthalpies obtained in our study with existing literature data demonstrates the high accuracy and broad applicability of our approach across various compounds.

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PHASE DIAGRAMS FOR THE Ga – S AND Mn – Ga – S SYSTEMS

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This work is devoted to the search for high-temperature modifications of gallium sulfides, which are very peculiar solids in structures. These solids are the layered GaS and sesquisulfide-family-phases (Ga_2S_3), which contain so-called stoichiometric vacancies in their structures. The study of these phases is important for the creation of new promising materials. In addition to traditional research methods (X-ray diffraction, synchrotron, differential thermal analysis), new methods of thermal analysis (TA) were also used: chromatographic thermographic analysis (CTA) [1] and differential thermal analysis with controlled vapor pressure of the volatile component (DTA-CVP). In the DTA-CVP-way of TA, the vapor pressure of the volatile component (sulfur) is established according to the known temperature dependence of the sulfur saturated vapor. This method is interesting because it allows, firstly, to monitor changes in the nature of phase transformations with varying pressure, and, secondly, to clarify the nature of some transformations. In particular, in this work, the use of CTA-CVP-way made it possible to select and justify the correct interpretation of the horizontal line at $t \approx 1006$ °C on the *T*-*x*-diagram of the Ga – S system.

The work confirmed recent results [2], according to which the γ-$Ga_{2+\delta}S_3$ phase with a cubic sphalerite-like structure is realized in a narrow temperature range of 878 – 922 °C; its composition was also refined (59.3 mol.% S). In addition, it has been established that at temperatures above 912 °C and at the compositions of small excess of gallium (up to ~1.0 mol %) relative to the stoichiometry of Ga_2S_3, two more modifications are realized: one of it has a wurtzite-type structure (β-Ga_2S_3, S.G. $P6_3mc$), the other one – is a daughter phase from the β-phase with a structure of lower symmetry (α-Ga_2S_3, $P6_1$). The last one achieves the congruent melting at 1109±2°C. The existence of the distectoid transformation β-$Ga_2S_3 \leftrightarrow \alpha$-$Ga_2S_3$ (~1040 °C) is argued. The fourth modification with a monoclinic structure (α'-Ga_2S_3, *Cc*) is stable in a region from RT up to ~1006 °C, its composition almost strictly corresponds to the Ga_2S_3-formula. The *T*-*x* diagram for the Ga – S system is presented and the areas of the above-mentioned phases are discussed.

The phase diagram for the Ga – Mn – S system was studied at low and moderate manganese concentrations (< 50 mol. % MnS) along the sections GaS – MnS, $Ga_{0.41}S_{0.59}$ – MnS, $Ga_{0.4}S_{0.6}$ - MnS and some others close to the last cross-section. The possibility of stabilizing each of the three high-temperature modifications of Ga_2S_3 with the doping by adding small specific amounts of manganese at certain cross-sections has been shown. This made it possible to obtain these modifications reproducibly and without the rapid quenching techniques using.

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MOLECULAR-LEVEL INSIGHTS TO STRUCTURE AND HYDROGEN BONDS NETWORK OF 1,4-DIOXANE AQUEOUS SOLUTION

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Dioxane is a widespread industrial solvent with a number of important properties. For example, dioxane is able to mix with water in any molar ratios. Because of this, the study of the structure of an aqueous solution of dioxane is of great scientific interest both from an experimental and theoretical point of view. The molecular dynamics method makes it possible to study the characteristics of a solution that are inaccessible to experimental techniques, and is also able to verify the correspondence of existing force fields to experimental results.

In this paper [1], a comparative analysis of hydrogen bond networks in an aqueous solution of 1,4-dioxane in the Smith's [2] and OPLS-AA/CM1A [3] force fields with the TIP4P water model is carried out. The total number of hydrogen bonds per oxygen atom and the specific number of water-water and dioxane-water hydrogen bonds are calculated, the results obtained are compared with experimental data on X-ray scattering [4]. The geometric criterion of percolation of the hydrogen bond network is introduced. The positions of the calculated percolation thresholds are compared with the experiment on broadband dielectric spectroscopy [5]. Calculations are carried out in the LAMMPS software package, the analysis of molecular dynamic trajectories is carried out using the TRAVIS and MDAnalysis software packages.

Both force fields describe well the experimental data [4] on the total number of hydrogen bonds per oxygen atom. However, differences in the hydrogen bond networks between the models used are observed only when analyzing the specific numbers of water-water and dioxane-water hydrogen bond. The underestimated values of the number of water-water bonds in the OPLS-AA/CM1A model are consistent with an underestimation of the enthalpy of dissolution [6]. Both force fields adequately reproduce the experiment [5] on the lower percolation threshold of the hydrogen bond network. Unlike OPLS-AA/CM1A, the onset of percolation in the Smith model is very close to the experimental upper percolation threshold. At low concentrations of dioxane, clusters of 2-3 dioxane molecules are present in solution, which is consistent with experimental data on X-ray scattering [4]. The OPLS-AA/CM1A force field demonstrates a less pronounced network of dioxane molecules at mole fractions ≥ 0.20.

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THERMOCHEMISTRY OF SODIUM, IRON, NIOBIUM PHOSPHATE NASICON SOLID SOLUTIONS

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Substances with the NASICON ($Na_4Zr_2(SiO_4)_3$) structure have drawn attention of researches due to their important technological properties, such as high ionic conductivity and low and controllable thermal expansion. Iso- and heterovalent substitutions in different crystallographic sites of the structure has led to the formation of a big family of NASICON-related compounds and solid solutions, containing elements with different oxidation states from +1 to +6. Despite that, the thermodynamic properties are reported for a limited number of them. Here we study thermodynamic stability and mixing properties of some representatives of this structural family, which was unknown before.

Solid solutions $Na_xFe_{0.5+0.5x}Nb_{1.5-0.5x}(PO_4)_3$ ($0 \le x \le 1$; $x = 2$) of NASICON structure (sp.gr. R3-c) were prepared *via* solid-state reaction and characterized by electron microprobe analysis, powder X-ray and neutron diffraction, and differential thermal analysis. The decrease of the *c* unit cell parameter prevails over the increase in *a* and *b* parameters, resulting in nonlinear decrease of the unit cell volume with Na content increasing.

Enthalpies of drop solution in molten sodium molybdate solvent ($3Na_2O\cdot4MoO_3$) at 700 °C were measured by high temperature oxide melt solution calorimetry and were used to derive the enthalpies of formation. Strongly negative enthalpies of formation from the elements and from the constituent oxides indicate high thermodynamic stability. The enthalpies of mixing, calculated from the equation:

$(1-x)Fe_{0.5}Nb_{1.5}(PO_4)_3 + xNaFeNb(PO_4)_3 \rightarrow Na_xFe_{0.5+0.5x}Nb_{1.5-0.5x}(PO_4)_3$, ($0 \le x \le 1$),

show a significant negative deviation from ideal mixing; intermediate compositions, are more energetically stable than a mixture of end members. Similar behavior with negative enthalpies of mixing (consistent with ordering) was found for the spinel system Fe_3O_4 – $Fe_{3/8}O_4$, for uranothorite $Th_{1-x}U_xSiO_4$ and for some other oxide systems. Negative mixing enthalpies and negative mixing volumes indicate short-range ordering of cations in the structure. Since no superstructure was observed in these phases, we can conclude that any ordering is only short-range.

ANALYSIS OF ACID-BASE RELATIONS OF OXIDES BASED ON HIGH TEMPERATURE OXIDE MELT SOLUTION CALORIMETRY

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Acid-base concepts have been applied to oxide systems in the solid, molten, and glassy states, as well as to vaporization processes. This work aims analyzing acid-base interactions in various oxide systems and their thermodynamics [1].

Experimental enthalpies of solution of a wide range of crystalline binary oxides in molten oxide systems of several compositions, obtained by oxide melt solution calorimetry at 700 and 800ºC, are systematized and analyzed. Oxides with low electronegativity of oxide forming atom (less than about 1.3 in Pauling scale), which are strong oxide ion donors (strong bases), show enthalpies of solution more negative than -100 kJ/mol. These include the alkali and alkaline earth oxides, for which the enthalpy of solution becomes more negative with decreasing electronegativity in the order Li, Na, K and Mg, Ca, Sr, Ba in both of the commonly used molten oxide calorimetric solvents: sodium molybdate and lead borate. The values in sodium molybdate are somewhat more negative than in lead borate, consistent with the former being a somewhat more acidic solvent. The second group is oxides with high electronegativity (> 2.1), including P_2O_5, SiO_2, GeO_2 and other acidic oxides. These oxide ion acceptors (acids) clearly compete with the complex anions in the solvent for bonding to oxygen. They dissolve more exothermically in the less acidic solvent (lead borate). The remaining oxides, a large group with electronegativity between 1.3 and 2.1, have heats of solution between +50 and -100 kJ/mol. with many close to zero. They correspond to amphoteric oxides.

Energetics of solution of oxides in multicomponent silicate melts at temperatures, higher than 1000°C is also discussed. The enthalpy of solution becomes more exothermic with decreasing melt acidity, reflecting a decrease of thermodynamic activity of silica as its concentration decreases.

These defined trends and a semiquantitative acid-base scale could be useful for understanding the thermodynamic driving forces for formation and decomposition reactions, involving oxide materials. We conclude, that the ionic model combined with the Lux-Flood theory of acid-base reactions provide a consistent and useful interpretation of the data and their application for understanding the thermodynamic stability of multicomponent oxide systems in solid and liquid states.

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PHASE EQUILIBRIUM IN PSEUDOTERNARY SYSTEMS OF DEEP EUTECTIC SOLVENTS WITH ESTERS AND ALCOHOLS FOR THE SEPARATION OF AZEOTROPIC MIXTURES

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Chemical substances used in various industrial sectors require a complex processing before their use. As a result, the development of high-purity separation technology is considered a key area of research and development in the chemical industry. As is known, esters and alcohols form azeotropic mixtures that are difficult to separate under standard conditions, which reduces the purity of the esters, negatively affects the quality of the final product, and significantly reduces the benefits of the esterification process. Conventional distillation makes it difficult to obtain high-purity esters, which necessitates the use of special methods for their separation. Therefore, there is a need to find an optimal method for separating the azeotrope of esters and alcohols.

The sustainable transition to cleaner production techniques over the last decade has projected deep eutectic solvents as alternative solvents to replace toxic volatile organic solvents especially in green extraction technologies. Deep eutectic solvents (DES) have been portrayed as the best analogue for replacing the traditional organic solvents or ionic liquids. The advantages compared to traditional ionic liquids are: nonreactive with water, simple to synthesize, the materials easily mixed and converted to liquid without further purification. DESs are mostly biodegradable and very cheap, because of the low cost of raw materials. These solvents can be adaptively tweaked for unique physico-chemical properties. They are binary hydrogen bonded mixtures of quaternary ammonium salts, or others with donors such as acids, amines, and alcohols. The eutectic mixtures reveal much lower the melting point of the mixture in comparison to the melting points of the individual components.

However, processes based on such newly developed solvents pose hindrances in industrial applicability due to lack of sufficient data for process design and scale up. The purpose of this study was to check choline chloride-glycerol-based DES as extractants to study their separation effects on alcohol-ester binary azeotropes.

The liquid-liquid equilibrium data at different temperatures (293.15, 313.15 K) for the DES-ester-alcohol system was generated. Deep eutectic solvents (DESs) exhibit good separation performance as extractants in extractive distillation. The binary azeotropes of esters (ethyl propionate, n-propyl propionate, ethyl acetate, n-propyl acetate, n-butyl acetate) and alcohols (ethanol, n-propanol, n-butanol) were separated using DES, and their separation performance was investigated.

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THERMODYNAMICS AND PHASE EQUILIBRIA IN THE Na^+, K^+ // $H_2PO_4^-$, Cl^- – H_2O SYSTEM

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Dihydrogen phosphates (MH_2PO_4) find extensive application across industrial domains, particularly in the context of mineral fertilizer production processes. Chlorides (MCl) commonly serve as reagents in industrial phosphate synthesis procedures [1–3]. However, the presence of chloride impurities in the final product is generally deemed undesirable. Therefore, the selection of crystallization conditions is of high significance.

The development and optimization of fertilizer synthesis processes necessitate the description of phase equilibria and thermodynamic properties of phases in multicomponent water-salt systems, across a wide range of compositions and temperatures. Such description can be obtained through thermodynamic modeling based on reliable experimental data. In this regard we examined the Na^+, K^+ // $H_2PO_4^-$, Cl^- – H_2O system and its subsystems in the temperature range from 0 to 100 °C.

We obtained new experimental data on liquid-solid phase equilibria in the Na^+, K^+ // $H_2PO_4^-$, Cl^- – H_2O system at 50 °C. During the experiment, accurate proportions of water, potassium and sodium dihydrogen phosphates, and chlorides were combined in containers with tightly sealed lids and agitated continuously until equilibrium was achieved. The investigated compositions were prepared and maintained in a thermostat. The composition of saturated solutions was determined based on the concentrations of Na^+, K^+, and $H_2PO_4^-$ ions, while the Cl^- ion content was determined by the difference. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was employed for measuring cation concentrations, and the phosphate anion was analyzed using the gravimetric method (in the form of $Mg_2P_2O_7$). The composition of the solid phase was determined through powder X-ray diffraction analysis (XRD).

Using new experimental results and critically selected literature data, we established a consistent thermodynamic description of the chosen system. The modeling was conducted following the CALPHAD architecture: binary subsystems were first described, then, based on them, ternary and quaternary systems. Calculations were performed within the framework of the Pitzer-Simonson-Clegg (PSC) model, taking into account acid-base equilibria. Acidity constants of orthophosphoric acid were calculated using the Helgeson-Kirkham-Flowers (HKF) equation based on parameters recommended in the works of Novikov et al. [4,5].

The resulting model accurately describes available experimental data on thermochemical properties, vapor-liquid and solid-liquid equilibria over a temperature range from 0 to 100 °C with high precision.

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HOW MOLECULAR SCALE ELECTRODE SURFACE STRUCTURE INFLUENCES ELECTRIC DOUBLE LAYER PROPERTIES

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The current knowledge regarding the influence of electrode surface characteristics on the behavior of the electric double layer (EDL) is limited. The structure of electrode surface affects the arrangement of ions in the electric double layer (EDL) on a molecular level. However, the description of EDL near rough electrodes is still challenging, especially by theoretical models. Recent molecular dynamics simulations proved that electrode surface morphology significantly impacts EDL structure and properties, like differential capacitance (DC) [1]. A fundamental understanding of the observed results will allow to select the optimal electrode structural properties required for the technological application based on EDL behavior.

To describe EDL near structured electrodes, we develop an analytical model based on the Modified Poisson-Fermi (MPF) equation that accounts for the ion separation driven by ion size asymmetry and ion steric repulsion from the electrode surface [2]. It is reflected by the additional term for the ion charge density, which includes the scale of surface roughness and the magnitude of ion separation. Then, we extend our model by using Bazant-Storey-Kornyshev theory [3] to account for the short-range electrostatic correlations and study the modifications of the overscreening regime.

The results of the proposed model qualitatively represent a wide range of molecular dynamics observations. Our model is the first to analytically predict a DC profile with more than two peaks, taking into account the reorientation of ions. We found that the DC curve transforms from a bell shape to a camel shape and back, depending on the electrode surface roughness. Moreover, we show that the electrode surface structure can lead to the breakdown of the overscreening regime if counterions are repelled on a level of electrostatic correlations.

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THERMODYNAMIC PROPERTIES OF THE SrO-Al_2O_3-SiO_2 SYSTEM STUDIED BY HIGH TEMPERATURE MASS SPECTROMETRY

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In recent years, researchers have paid increased attention to materials based on SrO–Al_2O_3–SiO_2 system, which have high melting points, thermal stability, and good strength properties, which make them promising for the fabrication of radiotransparent materials. Composite materials based SrO–Al_2O_3–SiO_2 system have high resistance to thermal shock, high chemical resistance, and stable dielectric properties, which make these materials suitable for manufacturing high-temperature antenna radomes and radio-transparent windows of highspeed aircraft with an operating temperature of at least 2300 K.

The most volatile components in the SrO–Al_2O_3–SiO_2 system are strontium oxide and silicon dioxide, which begin to transform into vapor at temperatures about 1800 K. The formation of solid solutions and thermally stable compounds in SrO–Al_2O_3, SrO–SiO_2, and Al_2O_3–SiO_2 binary systems, as well as in the SrO–Al_2O_3–SiO_2 ternary system, reduces the activity of the condensed phase components and increases the vaporization temperature.

The vaporization processes and thermodynamic properties of the SrO–Al_2O_3–SiO_2 were studied by high-temperature mass spectrometry on an MS-1301 mass spectrometer at an energy of ionizing electrons of 30 eV. The studied samples were evaporated from a twin Knudsen effusion cell made of tungsten. A sample was loaded into one of the compartment of the cell, and oxides of strontium or silicon alternately were loaded into the other. The cell was heated by electron bombardment, and the temperature was measured with an EOP-66 optical pyrometer.

An analysis of the mass spectra of the vapor over the studied samples and the energies of the appearance of ions in the mass spectra of the vapor indicate that, in the temperature range of 1950 to 2010 K, SiO, atomic strontium, and oxygen pass into the vapor according to equations of reactions:

$SrO\ (s) = Sr\ (g) + O\ (g)$ and $SiO_2\ (s) = SiO\ (g) + O\ (g)$

In this case, aluminium oxide accumulates in the condensed phase, which passes into vapor at a higher temperature.

The activities of strontium and silicon oxides were determined experimentally by differential mass spectrometry. For a region of a homogeneousmelt, using the Gibbs–Duhem equation, the activity values of aluminum oxide were calculated and the Gibbs energies and excess Gibbs energies were determined. The data obtained by us indicate that the studied system is characterized by a negative deviation from ideal behavior. This is due to the fact that the SrO–Al_2O_3– SiO_2 system is formed by oxides that differ in their acid-base properties. Strontium oxide is a typical basic oxide and forms thermally stable compounds with amphoteric aluminum oxide and acidic silica. In particular, in the SrO–Al_2O_3–SiO_2 system there are three-component compounds: anorthite, ($SrAl_2Si_2O_8$), gehlenite ($Sr_2Al_2SiO_7$), and $Sr_6Al_{18}Si_2O_{37}$.

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EXPERIMENTAL THERMOCHEMICAL STUDY OF PEROVSKITE-TYPE $CsPbX_3$ (X – Cl, Br, I) HALIDES AND THERMODYNAMIC MODELLING OF BINARY PHASE DIAGRAMS INVOLVING THESE COMPOUNDS

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Perovskite-type halides have received great attention in recent years due to high conversion efficiency obtained in solar cells based on such materials. However, despite very promising achievements their fundamental chemistry and physics is far from being completely understood. This is particularly true for thermodynamic properties of perovskite-type ABX_3 halides ($A=CH_3NH_3$, formamidinium, Cs, Rb, etc; B=Sn, Pb; X = Cl, Br, I). Moreover, reported results of DFT calculations aiming at estimating the stability of these materials often give controversial results. Therefore, experimental study of the formation thermodynamics of the ABX_3 halides is strongly required. This is especially important for assessment of the stability of these materials under particular working conditions as well as for thermodynamic modelling of phase equilibria. Therefore, the main aim of this work was to study the thermodynamics of formation of perovskite-type halides $CsPbX_3$ (X – Cl, Br, I) and their solid solutions and thermodynamic modelling of binary phase diagrams: CsX-PbX_2 and $CsPbX_3$-$CsPbX'_3$ (X, X′ – Cl, Br, I).

The standard formation enthalpies of $CsPbX_3$ (X – Cl, Br, I) halides and solid solutions at 298,15 K were measured by solution calorimetry. Enthalpy increments and constant pressure heat capacity were measured in the temperature range 298-800 K using drop-calorimetry. Standard entropies at 298,15 K were either calculated from the results of the EMF-measurements or estimated from the S^o_i vs. $\log(M_i)$ linear dependencies. Standard Gibbs free energies of $CsPbX_3$ (X – Cl, Br, I) halides were evaluated using the as-determined formation enthalpies and entropies. Mixing enthalpies, entropies and Gibbs free energies of $CsPbX_3$-$CsPbX'_3$ (X, X′ – Cl, Br, I) solid solutions were calculated as well. The trends in the variation of the thermodynamic functions with chemical composition and crystal structure of perovskite-type halides were analyzed and compared with available results of DFT calculations.

Also, binary phase diagrams CsX-PbX_2 and $CsPbX_3$-$CsPbX'_3$ (X, X′ – Cl, Br, I) were built using differential scanning calorimetry measurements. The resulting diagrams were compared with those available in literature. Their thermodynamic assessment was successfully carried out.

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STRUCTURAL-THERMODYNAMIC CHARACTERISTICS AND INTERMOLECULAR INTERACTIONS IN GLYCEROL MIXTURES

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Glycerol, like water, is a solvent with a spatial network of hydrogen bonds, which largely determines the structure and physicochemical properties of mixtures based on it. Compositions with glycerol are actively used in fundamental molecular research as cryoprotective mixtures; they dilute the “brine” formed during crystallization, preventing proteins from denaturing. Also, these mixtures protect cells from exposure to high pressure, i.e. are baroprotectors. Therefore, to predict the undesirable process of ice formation in biological objects at low temperatures, protein denaturation under conditions of high compression, a larger amount of data is needed on the properties of these mixtures. The molecular mechanisms by which cryoprotectants stabilize and protect molecules and cells, along with inhibiting ice formation, are not fully understood. To gain a greater understanding of these mechanisms, the influence of the cryoprotective mixture used, and its composition, it is necessary to know the properties of each component of these mixtures.

The report discusses the structural and thermodynamic characteristics of glycerol and mixtures based on it. The thermal and pressure characteristics of mixtures of glycerol with water and some alcohols are discussed.

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INVESTIGATION OF THERMODYNAMIC PROPERTIES OF RACEMATES OF PROTEINOGENIC AMINO ACIDS

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The paper presents the results of the study of DL-threonine and DL-tryptophan by high-temperature mass spectrometry. The study was carried out on a magnetic mass spectrometer MI1201, modified for thermodynamic studies. Commercial samples (Reachem; molar fraction >0.98) were loaded into a Knudsen molybdenum cell with a ratio of evaporation and effusion areas of ~400. Conclusions about the thermal stability of the chemicals during sublimation were made on a basis of the comparison of the IR spectra for the initial samples and their residues after the experiment.

Mass spectra were obtained and interpreted, and their agreement with the mass spectra from the NIST database was noted [1]. The dependence of the mass spectra on the temperature and energy of ionizing electrons was studied, on the basis of which it was concluded that the vapor of both compounds consists only of monomeric molecules. Saturated vapor pressures were measured using the Knudsen method. Their combination with the data of mass spectrometric measurements made it possible to recommend a saturated vapor pressure equation for each of the substances: $\ln(p, \mathrm{Pa}) = -(17.95 \pm 0.22)\cdot 1000/T + (39.02 \pm 0.48)$ in the range 371-454 K (DL- threonine); $\ln(p, \mathrm{Pa}) = -(21.25 \pm 0.20)\cdot 1000/T + (42.39 \pm 0.46)$ in the range 415-475 K (DL- tryptophan).

The obtained vapor pressures of the racemates are compared with the pressures for the corresponding chiral (L-) amino acids that we studied earlier [2, 3]. At the same temperature, the pressure of DL-threonine is about 2 times higher than the pressure of L-threonine, whereas the pressure of DL-tryptophan is about 3 times lower than the pressure of L-tryptophan. The enthalpy of sublimation of the studied racemates was determined by the method of the 2nd law of thermodynamics: $\Delta_{\mathrm{sub}}H°(298.15\ \mathrm{K}) = 150.3 \pm 4.3\ \mathrm{kJ\cdot mol^{-1}}$ (DL-threonine) and $\Delta_{\mathrm{sub}}H°(298.15\ \mathrm{K}) = 176.8 \pm 3.3\ \mathrm{kJ\cdot mol^{-1}}$ (DL-tryptophan). In both cases, these values exceed the enthalpy of sublimation of the corresponding L-forms of amino acids: $\Delta_{\mathrm{sub}}H°(298.15\ \mathrm{K}) = 146.0 \pm 2.1\ \mathrm{kJ\cdot mol^{-1}}$ (L- threonine), $\Delta_{\mathrm{sub}}H°(298.15\ \mathrm{K}) = 167.5 \pm 1.6\ \mathrm{kJ\cdot mol^{-1}}$ (L-tryptophan), obtained by the same method [2, 3]. The probable reason for the observed differences seems to be a stronger chemical bond in the crystals of racemates compared to the corresponding chiral amino acids.

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PFG NMR STUDY OF LOCAL DYNAMICS AND PHASE BEHAVIOR OF IONIC LIQUIDS RELEVANT TO PETROLEUM ASPHALTENE DISPERSION

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One of the major issues in crude oil production is ensuring successful flow both in upstream and downstream operations. Tendency of asphaltenes to aggregation followed by precipitation and deposition plays a crucial role in petroleum industry since these processes present severe problems during the production, recovery, and processing of crude oils and fossil hydrocarbon feedstocks. Consequently, understanding the phase behaviour of asphaltenes behind the destabilization processes is key factor affecting the overall handling of flow assurance problem.

Among the diversity of chemical agents developed to overcome the asphaltene deposition issue, the ionic liquids (ILs) attract special attention all the more. ILs are environmental friendly, recyclable and non-corrosive substances which can keep asphaltene molecules in dispersed state so it can be utilized as a green chemistry alternative to the common chemical dispersants (e.g. aromatic solvents, surfactants such as octylphenols or DBSA etc). Despite some progress in this field, we still know a little about the mechanisms of IL and asphaltene interactions in native state (i.e. when no flocculant is added to asphaltene solution) or dynamics of aggregates and their phase behavior in presence of IL.

In this report we demonstrate the results of new PFG NMR study of imidazolium-based ILs ([BMIM]BF_4, [BMIM]TFSI) both in their native state (model solutions in $CDCl_3$, Fig.1a) and being added to model asphaltene solutions (Fig.1b). The concentration dependence of chemical shifts and diffusion coefficients of the components were measured, the local dynamics and phase behaviour of asphaltene nano-/macroaggregates were elucidated in presence of small amounts of ILs. The results obtained showed complex associative phase behavior of ILs in native state and obvious dispersing effect of ILs on asphaltenes visible through the pronounced mobility of aggregates. The latter was first observed for the native asphaltene solution and ILs with relatively short alkyl chain of imidazolium cation.

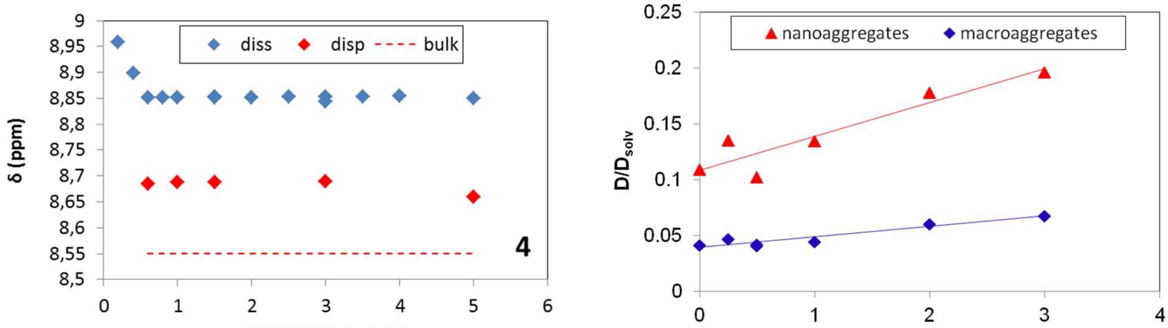

Figure 1. Concentration dependence of ^{1}H chemical shift of 4 position of imidazolium cation in dissolved and dispersed states (a); asphaltene aggregates mobility increase in presence of IL (b)

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THERMODYNAMIC PROPERTIES OF RE TITANATES $RE_2Ti_2O_7$ WITH PYROCHLORE STRUCTURE

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Rare-earth titanates of the composition $RE_2Ti_2O_7$ (RE=La-Lu, Y), which have congruent melting temperatures above 1800°C, draw attention as components of promising high-temperature materials. Titanates with the structure of pyrochlore (RE=Sm-Lu, Y) attract the greatest interest and their phase diagrams, structure and magnetic properties was published. Information on thermochemical properties is presented in experimental [1] and model [2] studies of enthalpy of formation. The numerical data on heat capacity in the wide temperature range for whole pyrochlore set of $RE_2Ti_2O_7$ are not available in the literature. Investigation of low temperature heat capacities of Er, Tm and Lu pyrochlores by adiabatic calorimetry were published in [3,4]. High temperature heat capacity of $RE_2Ti_2O_7$ was studied mainly by DSC [e.g. 5].

Here we present the results of heat capacity measurements by three different calorimetric methods (relaxation, adiabatic and DSC) in the range 2-1800 K. Three $C_p(T)$ curves were docked and smoothed using polynomials and CpFit software. Thermodynamic properties (entropy and enthalpy change) were evaluated from smoothed $C_p(T)$ values in the studied temperature region.

Peculiarities of heat capacity curve for lutetium titanate and gadolinium titanate made it difficult extraction of the Schottky anomalies for paramagnetic RE compounds below the room temperature using the Westrum “volumetric method”.

Gibbs energy $\Delta_f G_{ox}(T)$ of reactions of RE titanates formation from oxides
$RE_2O_3 + 2TiO_2 = RE_2Ti_2O_7$ in the high temperature region were calculated using the literature values and thermodynamic functions from this study to assess thermodynamic stability.

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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF REMgAl$_{11}$O$_{19}$ (RE=La,Pr,Nd, Sm) HEXALUMINATES WITH MAGNETOPLUMBITE STRUCTURE

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REMg hexaaluminates (REMgAl$_{11}$O$_{19}$) considered in the last years as the candidate to materials for Thermal Barrier Coatings (TBC) [1] due to the unique combination of thermal and mechanical properties – high melting temperature, low thermal conductivity, thermal expansion compatible with superalloy and TGO values, low porosity and shrinkage, toughness. In addition, REMg hexaaluminates must be resistive to CMAS corrosion. This combination of properties depends, particularly, on the composition and crystal structure of these compounds.

Studied REMg hexaaluminates (RE=La, Pr, Nd, Sm) were synthesized by sol-gel technology with the following step-wise calcination finally at 2000 K during 4 hs. Specimens were characterized by XRD (Bruker D8 Advance) and scanning microscopy (Tescan Amber) with EDX analysis. Thermal behavior of RE-Mg hexaaluminates was studied using DSC Netzsch 404F1 Pegasus up to 1800 K and no thermal effects related to phase transitions were found.

Heat capacities of REMgAl$_{11}$O$_{19}$ were measured by relaxation, adiabatic and differential scanning calorimetry in the temperature range 2-1800 K. Dependences obtained by relaxation calorimetry and DSC were docked to adiabatic curve and smoothed jointly. Thermodynamic properties (entropy, enthalpy change and reduced Gibbs energy) were calculated using the smoothed data. High-temperature heat capacities were presented by Maier-Kelley equation.

The entropy contribution to the Gibbs energy of the formation of hexaaluminates from oxides following the reactions

$0.5\ RE_2O_3 + MgO + 5.5\ Al_2O_3 = REMgAl_{11}O_{19}$

$0.5\ RE_2O_3 + MgAl_2O_4 + 4.5\ Al_2O_3 = REMgAl_{11}O_{19}$

was estimated using the literature data [2-4] and the values obtained in this work.

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DIFFERENT STATES OF WATER IN α- AND β-CYCLODEXTRIN HYDRATES

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Cyclic macromolecules consisting of 6, 7, or 8 glucopyranose units, respectively are α-, β- and γ-cyclodextrins (CDs). These units form hollow truncated cone cavity with hydrophilic exterior and hydrophobic interior, which can include a wide range of guest molecules, thereby forming various host-guest inclusion complexes. These inclusions may beneficially change of CD physicochemical characteristics such as solubility, thermal stability, volatility, resistance to oxidation, visible and UV light, etc. Because of these properties CDs are widely used in analytical chemistry, catalysis and also in pharmaceutical, food and cosmetic industries. Water plays an important role in CDs inclusion complexes formation, since the process of complex formation is essentially a replacement reaction of water molecules located in CD cavities by hydrophobic guest molecules. Meanwhile, quantitative data on equilibria between CDs and H_2O are very scarce and contradictory, which makes it difficult to produce high-quality materials.

The purpose of this work is a comprehensive study of the α- and β-CD hydrates dehydration processes by static method with glass membrane-gauge manometers. The measurements have been realized in the wide intervals of temperature ($313 \leq T/\mathrm{K} \leq 483$), pressure ($0.5 \leq p/\mathrm{Torr} \leq 760$) and composition ($\mathrm{CD}{*}n\mathrm{H_2O}$, $0.2 \leq n \leq 9.58$). The accuracy of measurements for used setup was 0.5 Torr, 0.5 K and 0.01 formula units in the values of pressure, temperature and solid phase composition, accordingly [1]. ^{1}H NMR study (Bruker AVANCE II+ 300 WB) was performed to confirm the results obtained.

As a result of this study thermal stability of investigated compounds was established, temperature dependences of pressure for dehydration processes were obtained (five types of dehydration processes for α-CD and two for β-CD were studied), enthalpies and entropies of dehydration were determined and Gibbs energy change in the process of binding water with CDs was calculated. On the base of information obtained the conclusions about the nature of the interactions between host (CDs) and guest molecules (water) were drown. The main results on α-cyclodextrin hydrates are published in [2-3].

The accumulation of quantitative information about the dehydration processes of CDs hydrates will allow one to synthesize functional materials with desired properties in the future.

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INFLUENCE OF TEMPERATURES ON THE SALTING-OUT OF BUTYRIC ACID FROM ITS AQUEOUS SOLUTIONS BY POTASSIUM DIHYDROGEN PHOSPHATE

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The production of biobutyric acid is complicated because of its low content in fermentation solutions (<80 g/L). That requires searching for effective methods of its concentration and extraction. Butyric acid has a high boiling point, so the use of rectification to separate butyric acid is unprofitable. A simple and cheap method of concentration is the salting-out of butyric acid using inorganic salts. Combining salting with liquid-liquid extraction (SOE – salting-out extraction) leads to an increase in the efficiency of butyric acid extraction. Interest in this method is growing every year, as it allows the extraction of hydrophilic products from aqueous solutions using non-toxic reagents. To optimize the salting-out process, it is necessary to have detailed information on the phase states occuring in mixtures of water and butyric acid under the action of salts at different temperatures. Analysis of such data allows one to give recommendations on the conditions for carrying out concentrating and isolation to achieve the maximum efficiency of these processes. The aim of this work was to reveal the phase behavior of mixtures of water and butyric acid under the action of potassium dihydrogen phosphate in a range of 10.0-90.0°C.

The phase equilibria in the mixtures of the components of the $KH_2PO_4-H_2O-C_4H_8O_2$ ternary system were studied in glass ampoules under vapor pressure using the visualpolythermic method. The following phase states were carried out in these mixtures: homogeneous state (liquid), solid–saturated solution (liquid-solid equilibrium), two-phase liquid (liquid-liquid equilibrium) and monotectic (liquid-liquid-solid equilibrium). The solid phase of saturated solutions at all temperatures was the individual salt. Polytherms of phase states were plotted for all sections.

The dependence of the composition of mixtures corresponding to the critical solubility points of the liquid–liquid equilibrium on temperature was determined. The compositions of critical solutions were determined by the phase volume ratio method. An increase in temperature leads to the fact that the content of potassium dihydrogen phosphate and water in critical solutions increases, and the content of butyric acid decreases.

Polytherms of phase states and critical curves were used to construct isothermal phase diagrams of a triple system at 10.0, 25.0, 40.0, 60.0, 90.0°C. Isotherms at all temperatures correspond to the salting out of a binary homogeneous system. The fields of saturated solution and the field of delamination with critical point K adjoined the sides of the monotectic triangle. With an increase in temperature, the size of the monotectic triangle and the adjacent stratification fields increase slightly, and the fields of saturated solutions decrease, therefore, an increase in temperature increases the salting effect of potassium dihydrogen phosphate on a mixture of water and butyric acid.

The coefficients of distribution K_D of butyric acid were calculated as the ratio of its concentrations in the organic and aqueous phases of the monotectic state at the specified temperatures. The effect of salting out butyric acid from aqueous solutions with potassium dihydrogen phosphate increases with increasing temperature ($K_D = 9$ at 10.0°C, $K_D = 50$ at 90.0°C). Obviously, with increasing temperature, the interaction of components in the water–butyric acid binary system weakens due to the destruction of hydrogen bonds and the concentration of salt in the aqueous phase of the monotectic state increases. So, potassium dihydrogen phosphate can be recommended for the effective salting-out of butyric acid from aqueous solutions.

INVESTIGATING STRUCTURAL MODIFICATIONS IN MODEL LIPID MEMBRANES WITH DRUGS VIA MAS NMR SPECTROSCOPY

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One of the paramount endeavors within the realm of contemporary physical chemistry involves elucidating the structural characteristics, conformational mobility, and interactions of pharmacological agents with cellular membranes. The execution of such endeavors is crucial in the context of medicinal compound modification aimed at the mitigation of adverse effects. Research delineated in reference [1] posits that the side effects associated with certain non-steroidal anti-inflammatory drugs (NSAIDs) may be intricately linked to their specific interactions with phospholipid membranes. Alterations in the structure, dynamics, and fluidity of these membranes can precipitate the malfunction of proteins localized within these structures. Nuclear Magnetic Resonance (NMR) spectroscopy, employing magic angle spinning (MAS), emerges as a significant methodology for the examination of membrane architecture. The study under discussion presents an investigation into the structural peculiarities of model lipid membranes, specifically phosphatidylcholine (POPC)-based, in the milieu of small molecular entities, namely fenamates (including mefenamic, tolfenamic, and flufenamic acids). A meticulous analysis utilizing 2H, 31P, and NOESY MAS NMR spectral data facilitates a precise quantitative evaluation of alterations in the order parameters and the lengths of lipid chains within the membrane, in addition to ascertaining the loci of small molecular inclusions within the lipid bilayer. Observations indicated an augmentation in the average chain length of POPC from 12.4 Å to 12.6 Å and 12.5 Å in the presence of tolfenamic and flufenamic acids, respectively, whereas the presence of mefenamic acid exhibited no significant impact on the aforementioned characteristic [2]. Furthermore, it was discerned that all three fenamates are situated proximal to the head group of the POPC lipid, with flufenamic acid demonstrating a deeper penetration into the lipid bilayer via its anthranil fragment, in contrast to tolfenamic and mefenamic acids. The variance in interaction dynamics of fenamates with POPC membranes mirrors their distinct chemical attributes and pharmacological profiles. This insight may further contribute to the development of strategies aimed at the modification of NSAIDs to minimize their adverse effects.

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SYNTHESIS AND THERMOPHYSICAL PROPERTIES OF ONION-LIKE CARBON NANOPARTICLES

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Carbon nanoflakes (CNFs) are a promising carbon nanomaterial that can be used as a catalyst, an adsorbent, or as a matrix for stabilization of oxide nanoparticles, including Ln_2O_3 used as contrast agents for computed tomography [1]. CNF particles transform into onion-like carbon (OLC) particles under spark plasma sintering (SPS) treatment [2]. The present work is devoted to the synthesis of OLC particles, their heterosubstituted analogies, and core-shell structures $Ln_2O_3@C$ produced *via* SPS of CNFs, N-, P-, Si-CNFs and Ln_2O_3 deposited on the CNF surface.

Carbon nanoflakes (CNFs) were synthesized by pyrolytic decomposition of hexane at 900 °C in the presence of a MgO template. MgO was removed by HCl. Nanoparticles of Gd_2O_3 were produced by impregnation of CNFs with $Gd(NO_3)_3 \cdot 6H_2O$ and subsequent decomposition under N_2 atmosphere. A Labox-625 (Sinterland, Japan) apparatus was used for the SPS of samples. The SPS conditions were 1100 ºC and 30 MPa. The CNFs before and after SPS were characterized by elemental analysis, thermogravimetry, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The CNF, N-, P-, Si-CNF particles replicated the MgO form and contained 7-15 carbon layers. According to XPS, the contents of N, P and Si atoms in the composition of +N-, P-, and Si-CNFs were 10.0, 0.1 and 8.1 at. %, respectively. The contents of the N and Si atoms were 1.2 and 0.1 at. % after SPS, respectively.

The heat of combustion, standard enthalpies of combustion $\Delta_c H^0_{298}$ and formation $\Delta_f H^0_{298}$ of CNFs, OLC and their heterosubstituted analogies were determined for the first time by isothermal bomb calorimetry.

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SEPARATION EFFICIENCY OF THE 1-BUTANOL – 1-BUTYL FORMATE SYSTEM BY DES BASED ON CHOLINE CHLORIDE

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The separation of azeotropic mixtures is an important objective in chemical technology. Deep eutectic solvents (DES) have good prospects in optimizing the separation processes of aromatic-aliphatic and alcohol-hydrocarbon azeotropic mixtures using the liquid-liquid extraction method [1,2]. The current study investigated the efficiency of extracting 1-butanol from the 1-butanol – 1-butyl formate system using different DES based on choline chloride (ChCl). The following substances were selected as hydrogen bond donors: urea (Ur), glycerol (Gl), ethylene glycol (EG) and glutaric acid (Glu). Liquid-liquid equilibria (LLE) compositions for the systems 1-butanol – 1-butyl formate – DES were analyzed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy as in our previous studies [3]. The distribution coefficients and selectivity values were calculated. Based on dependency analysis of the selectivity values on 1-butanol mass fraction (Figure 1) we can conclude that the DES (ChCl/Ur) and DES (ChCl/Gl) demonstrated the highest efficiency in separating the 1-butanol – 1-butyl formate system. LLE was calculated using the Non-Random Two-Liquid (NRTL) equation, which demonstrated pretty well consistency between experimental and calculated data.

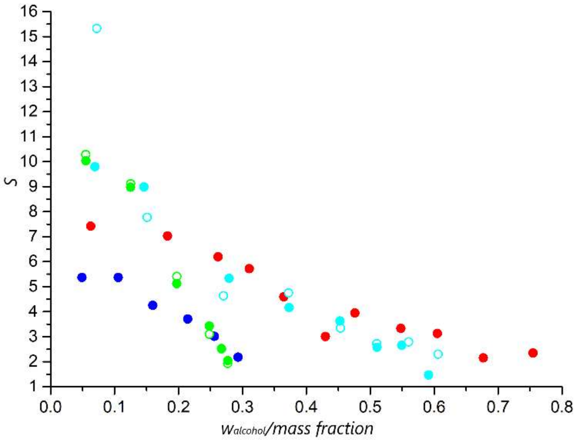

Figure 1. Dependences of the selectivity values (*S*) on 1-butanol mass fraction in the systems : 1-butanol – 1-butyl formate – DES (ChCl/Glu) (●) at 313.15 K, 1-butanol – 1-butyl formate – DES (ChCl/Ur) (●) at 313.15 K, 1-butanol – 1-butyl formate – DES (ChCl/EG) (○) at 293.15 K and (●) at 313.15 K, 1-butanol – 1-butyl formate – DES (ChCl/Gl) (○) at 293.15 K and (●) at 313.15 K

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ENTHALPY-HOMOTACTIC PARAMETERS OF INTERACTION FOR *UROTROPINE* AND SOME OTHER BIOACTIVE NITROGEN-CONTAINING CYCLIC NON-ELECTROLYTES AS SOLUTES IN D_2O AND H_2O AT 298.15 K

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For physical chemistry of aqueous solutions, the bioactive hexamethylenetetramine (HMTA) or *urotropine* is of special interest due to its cage-like or aminal molecular structure (Fig. 1) in which hydrophilic >N̈– and hydrophobic $>CH_2$ moieties have marked competitive influence on the structure of the hydration shell formed. To study the nature of this influence, we used jointly the methods of precision calorimetry of mixing/dilution and H_2O-by-D_2O solvent isotope substitution [1-3]. The enthalpy-homotactic coefficients of pairwise, h_{22}, and triplet, h_{222}, interactions between hydrated solute molecules, being computed using the excess thermodynamic function concept (the McMillan-Mayer formalism), are presented in Table 1.

Table 1. Enthalpic coefficients h_{22} and h_{222} in aqueous HMTA solutions at $T = 298.15$ K

Parameter	Source	H_2O	D_2O	$H_2O \rightarrow D_2O$
h_{22} /(J·kg·mol^{-2})	Our data	833 ± 28	1082 ± 39	249 ± 48
	Reference [4]	872 ± 62	–	–
h_{222} /(J·kg^2·mol^{-3})	Our data	128 ± 20	156 ± 29	28 ± 35

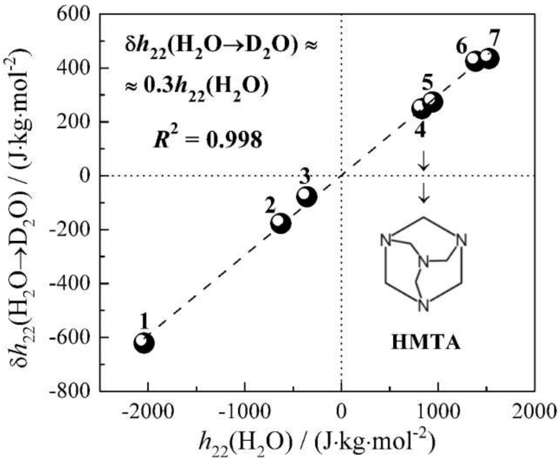

Figure 1. The correlation between enthalpic coefficients of pairwise solute – solute interactions in water and corresponding solvent H/D isotope effects for solutions of HMTA (**4**) and *N*-alkylated mono- and bicyclic derivatives of urea at 298.15 K [2,3]: **1** – *mebicar* (tetramethyl*bis*urea), **2** – *mebicaret* (*cis*-dimethyldiethyl*bis*urea), **3** – *albicar* (*trans*-dimethyldiethyl*bis*urea), **5** – dimethylethyleneurea, **6** – dimethylpropyleneurea, **7** – *bicaret* (tetraethyl*bis*urea).

The large and positive values of h_{22} and h_{222} in H_2O and D_2O are owing to a partial overlapping of solute hydrophobic hydration shells. As seen from the table, this phenomenon is stronger pronounced in heavy water indicating a higher-ordered hydration structure in D_2O. A close-to-linear function of $h_{22}(H_2O \rightarrow D_2O)$ *vs.* $h_{22}(H_2O)$ for HMTA and some other proton-accepting cyclic compounds (Fig. 1) confirms the hypothesis of the differentiating effect of a solvent isotopic substitution on thermodynamic characteristics of solute – solute interactions.

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THERMODYNAMIC ANALYSIS OF SYSTEMS CONTAING LIQUID CRYSTALS

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Liquid crystals (LC) are widely used in electro-optical devices and in display technologies. Liquid crystalline materials (LCM) are multicomponent mixtures having a wide temperature range of the certain mesophase type. For modelling of LCM composition it is necessary to know the parameters of intermolecular interaction of components. Unfortunately, thermodynamic description of systems containing LC is restricted by the ideal solution model.

More than 250 nematic (smectic-nematic, smectic) LC – non-mesogen systems were investigated. T-x-diagrams and solubility curves were obtained by DTA, visual analysis, polarizing microscopy and solubility methods. Solubility curves of LC that belongs to different homologues series (cyanobiphenyls, phenylcyclohexanes, phenylbenzoates, benzylidenanilines, benzoic acids, cholesteryl esters) were investigated. Solvents of different series (alkanes, cyclohexane, aromatics, chlorinated compounds, alcohols, esters, ethers, acetone and acetonitrile) were used. Tests for miscibility of components were made. Positive deviations from ideality ($\gamma_i > 1$) were revealed in the majority of systems. Complete T-x diagrams were obtained for systems of LC with tolane, phenyl benzoate, p-xylene and 1,4-dioxane.

The thermodynamic models based on the solubility parameter approach (Hildebrand (δ_i) and the Hansen (δ_{di}, δ_{pi}, δ_{hi}) solubility parameters, the Flory-Huggins equation) were applied for the demixing and solubility curves calculation. Molar volume, vaporization enthalpy and the solubility parameters of mesogens were estimated basing on different group-contribution schemes. Data for prediction were taken from [1]. The solubility of LC at 298 K was correlated with the radius R_a [2]: $R_a^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2$,
where 1 - LC, 2 - non-mesogen (solvent).

The UNIFAC models were applied for the activity coefficients estimation too. Thermodynamic analysis of phase diagrams was made.

Restrictions and advantages of the considered thermodynamic methods are discussed. Correlations between alkyl chain length of LC and their solubility in solvents of different polarity are determined.

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WIDOM LINES IN TRADITIONAL AND “COMPLETE” SCALING MODELS

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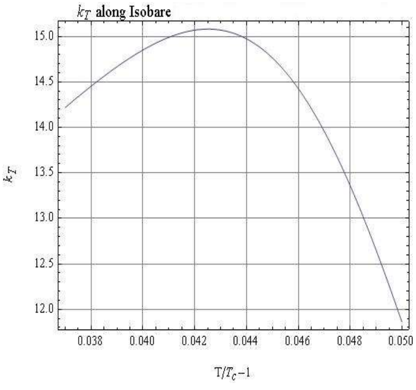
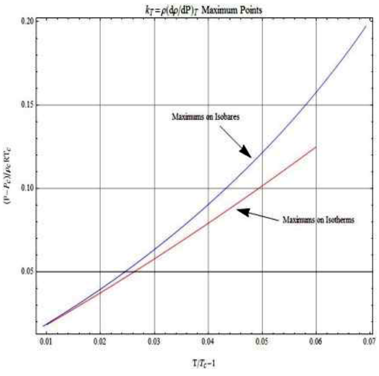
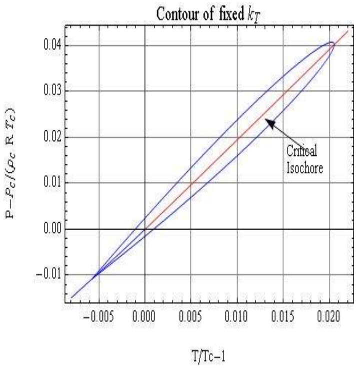
This research deals with the behaviour of such thermodynamic properties as isothermal compressibility $k_T = \rho^{-1}\left(\partial\rho/\partial P\right)_T$, isobaric heat capacity C_P and thermal expansion coefficient $\alpha_P = -\rho^{-1}\left(\partial\rho/\partial T\right)_P$ in the supercritical region of a one-component fluid in the vicinity of liquid-gas critical point. A known assertion is that in one-phase region there is a line, which separates the gas-like states from fluid-like states, called as Widom line. Originally, such line was identified with a line of maxima of fluctuations correlation length or equivalently with the continuation of the critical isochore in supercritical region. Since this characteristic is not directly measurable, it seems more preferably to investigate the properties mentioned above. Thus, we studied the behaviour of these thermodynamic properties along various isobars, isotherms and critical isochore above in supercritical region in the scope of both traditional scaling and in the framework of so-called complete scaling [1]. One of the goals of present study is to distinguish the difference between two approaches and to find the system where this distinction can be verified experimentally. All studied properties demonstrate non-monotonic behaviour on isobars and isotherms, namely, they possess maxima and the positions of these specific points differ from each other. A well-known parametric Linear Model [2] has been used to derive conditions determining maxima locations in explicit form. Due to simplicity of developed approach most of calculations maybe carried out analytically. For example, contours of fixed k_T can be easily plotted as a function of temperature or pressure. Such contours are very useful for light scattering experiments since they determine the lines of constant intensity of scattered light. Behaviour of compressibility k_T on isobare and is shown below (the similar picture takes place on an isotherm). Second picture presents the maxima curves on isobars and isotherms. Third picture demonstrates the typical contour of fixed compressibility k_T .We introduced also the ratio $\left(\partial k_T/\partial\tau\right)_P \big/ \left(\partial k_T/\partial P\right)_T$. This ratio is equal to zero at maxima on isobares and tends to infinity at maxima on isotherms. On the other hand this value is just $-\left(\partial P/\partial T\right)_{k_T}$, i.e. the temperature derivative of the pressure along the contour of fixed k_T . Hence, a «cricondenbar» of the contour coincides with maximum on isobare whereas a «cricondenterm» coincides with maximum point on an isotherm. Asymptotically close to critical point curves of maxima merge.







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OBTAINING A COMPOSITE MATERIAL FROM THERMODYNAMICALLY INCOMPATIBLE POLYCARBONATE AND POLYETHYLENE TEREPHTHALATE THROUGH THE DISPERSION PROCESS USING THE METHOD OF SEDS

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Polymeric materials and products made of these materials are widely used in all industries, but not all polymers have the necessary combination of properties. Therefore, creating new promising polymer composites by blending polymers is a relevant task. As a result, materials with the required combination of properties can be obtained. For example, the use of composite materials in the aviation industry significantly reduces material consumption and manufacturing complexity.

Currently, one of the promising directions for the processes of blending and dispersing of polymeric materials is the use of a fairly large group of methods involving processes with the participation of supercritical fluid media and supercritical carbon dioxide. Unlike traditional blending and grinding methods, these highly sensitive to the process conditions technologies allow obtaining homogeneous materials with certain physicochemical properties and particle sizes.

The discussed task is a continuation of the previous investigations [1–3], which consider obtaining composite materials using supercritical fluid technologies.

Thus, the results of the joint dispersion of polycarbonate and polyethylene terephthalate polymer blends, carried out in the pressure range of (9–20) MPa at temperatures of (313–333) K using the SEDS method, are presented.

The calorimetric studies of polyethylene terephthalate/polycarbonate waste blends reveal that, for all blends and pure polymers obtained through the SEDS method, the specific heat of melting exceeds these values for blends and individual polymers obtained by melt blending. This indicates that in this case, better conditions are created for the crystallization process, extending to the crystallization of amorphous polycarbonate and polyethylene terephthalate.

Based on the investigation of melting-crystallization-melting diagrams of the dispersion process samples, it can be concluded that, for all pairs of polymers, the heat of melting for blends obtained by SEDS method is significantly higher than the heat of melting for blends obtained by melt blending. It can also be noted that mixing within the SEDS method leads to an increase in the degree of crystallinity and, consequently, an improvement in the structure of the polymer matrix.

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WHY ETHALINE CANNOT BE REGARDED AS A DEEP EUTECTIC SOLVENT?

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Deep Eutectic Solvents (DESs), binary mixtures of a hydrogen bond donor and a hydrogen bond acceptor, are currently in the focus of solution chemistry due to their excellent solvent properties, competitive cost, and low environmental impact.[1,2] According to common wisdom, DESs exhibit exceptional freezing-point depression. Surprisingly, this is not the case for one of the most studied "DES", namely ethaline, the 1:2 molar ratio mixture of choline chloride (ChCl) with ethylene glycol (EG). Its freezing point was believed to be equal to 207 K.[3] However, when working with pure unhydrous ethaline we noticed partial crystallization of ChCl at already 293 K.

To clarify these contradicting findings, we investigated the phase behaviour of {ChCl + EG} mixtures for ChCl mole fractions (x_{ChCl}) less than 0.333 and temperatures below 323 K by determining melting points with differential scanning calorimetry.[4] We show that ethaline, that is usually believed to be the composition of the eutectic point, actually lies in the ChCl-saturated region of the {ChCl + EG} phase diagram. The real eutectic point was found to be the 1 : 4.85 molar ratio of ChCl : EG ($x_{\mathrm{ChCl}} = 0.171$) with a melting temperature of 244 K. Thus, neither from its specific composition, nor from the observed melting-point depression for {ChCl + EG} mixtures, ethaline can be considered a ''DES''. Surprisingly, although ChCl is a strong electrolyte that dissociates almost completely in water,[5] solutions of ChCl in EG exhibit the phase diagram of an ideal binary mixture of two non-electrolytes.

To shed light on this unexpected behavior we studied EG solutions of ChCl up to saturation at 298 K using dielectric relaxation spectroscopy. It turned out that the effective solvation number of ChCl is negligible. Up to ~2 M solutions are dominated by contact ion pairs before smoothly blending into the behavior of a "solvent-lubricated" molten salt. The implications of these findings for the phase behavior of ethaline and its solvent properties are discussed.

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SILK FIBROIN ADSORPTION FILMS ON AIR-WATER INTERFACE

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Bombix mory silk fibroin (SF) is one of the most frequently used proteins in biotechnology [1,2]. Numerous SF applications starting from the enzyme immobilization to controlled drug release and the scaffold formation for tissue engineering have been described in literature [2]. The characterization of the surface properties of SF solutions is mainly limited to measurements of the dynamic surface tension and surface elasticity close to equilibrium [3]. At the same time, there is a lack of information on the formation mechanism of the adsorption layer and the changes of its structure at the approach to equilibrium.

The investigation of these processes by measurements of the kinetic dependencies of the dynamic surface elasticity and surface pressure together with the simultaneous determination of the morphology and compression isotherms of SF adsorption layers was performed. The dynamic surface elasticity of SF solutions exceeds significantly the values of previously studied protein solutions and reaches up to 220 mN/m. It was shown by atomic force microscopy measurements that unlike globular proteins, SF tends to form more varied surface aggregates like threads, ribbons and branched tree-like structures. The formation of supramolecular structures at the interface results in a variety of mechanical properties of the adsorption layer. At the beginning of adsorption an almost two-dimensional network of SF aggregates is formed at the solution – air interface. In the course of adsorption and with the increase of surface pressure the layer becomes more heterogeneous and thicker. The transition from an almost 2D structure to a 3D layer structure can occur rather abruptly at surface pressures close to 15 mN/m in the course of adsorption layer compression in the concentration range 0.005 – 0.02 mg/l. At the same time, the structure and properties of SF adsorption layers depend not only on the surface pressure but are history-dependent. The fast adsorption at bulk concentrations higher than 0.02 mg/l results in the formation of a less rigid 3D layer with a lower surface elasticity than at lower SF concentrations.

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PHASE TRANSITION THERMODYNAMICS OF β-DIKETONATE METAL COMPLRXES FOR GAS-PHASE DEPOSITION PROCESSES

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The most basic application of β-diketonate metal complexes is as precursors for the formation of film materials in gas-phase chemical deposition. Quantitative data on volatilization (temperature dependences of saturated vapor pressure) and thermal behaviour in the condensed phase (thermal stability, phase transitions) of the precursors used are of great importance for efficiency of these processes. Any new thermal and thermodynamic data on any compound from β-diketonate class have not only practical significance for technological processes using the studied precursor, or fundamental – for the accumulation of reliable thermodynamic data, but also form the platform for searching for correlations. In turn, the latter are necessary as a tool for both diagnosing the quality of available data and assessing lacking properties. A striking example of hard-to-access data are the temperature dependences of saturated vapor pressure and thermodynamic functions of vaporization or sublimation for silver-containing complexes due their extremely high light sensitivity and thermal instability. At the same time, the demand for these complexes is great and constantly growing, since they can be used in gas-phase processes for the formation of coatings and silver nanoparticles, for example, on the materials of modern implants as components of heterostructures with an active antibacterial surface [1].

The focus of this work is one of the few effective precursors – (hexafluoroacetylacetonato)(cyclooctadiene-1,5)silver, $[Ag(cod)(hfac)]_2$. The thermodynamic properties (sublimation and vaporization) of this compound was assessed with using an approach based on correlations and generalizations [2–4]. The approach was developed with involving new data on various metal complexes, including isoligand compounds of other metals (I), [Cu(cod)(hfac)] and [Ir(cod)(hfac)] [5,6].

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ANALYSIS OF CALORIMETRIC CURVES OF TINI ALLOY WITH MULTIPLE MARTENSITIC TRANSFORMATIONS

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Shape memory alloys (for example, TiNi) are widely used as functional materials in various industries [1-3]. A possible way to increase the strength and functional properties of the TiNi alloy is thermal cycling (TC). The features of structure formation during aging have been studied quite fully; in particular, various scientific groups have carried out studies on the effect of temperature and time of isothermal annealing on the size, morphology and distribution of particles of the Ti_3Ni_4 phase, therefore, the study of the effect of aging on the microstructure and properties of the TiNi alloy with preliminary thermal cycling is of great interest, since increasing the strength and wear resistance of the material is a very urgent task. The use of structure modification methods makes it possible to reduce the grain size with the creation of an ultrafine-grained (UFG) or nanocrystalline (NC) structure in these alloys. Research was carried out on Ti-50.8 at.% Ni alloy in coarse-grained (CG) and UFG states, after aging in the temperature range 250...400 °C after TC 0...500. As a result of such processing, the generation and accumulation of dislocations in the structure occurs with an increase in the number of cycles in both the CG and UFG states. After the maximum number of cycles and annealing in the range of low-temperature and high-temperature aging, an additional increase in the dislocation density occurs, and also, in certain areas of the structure in the UFG state, the presence of aging particles can be detected. According to the data obtained in the coarse-grained state, during direct martensitic transformation, one distinct exothermic peak appears on the DSC curves. During the reverse martensitic transformation, an endothermic peak is observed, associated with the emergence of a high-temperature austenitic phase B2 from the martensitic phase B19'. After thermal cycling with n=100 cycles, a peak from the intermediate phase R during direct martensitic transformation and a decrease in the temperatures of martensitic transformations (M_s, A_f) are observed. After the maximum number of cycles, multidirectional temperature changes were observed, including a slight decrease in the temperature of the beginning of direct transformation (M_s) and the end of reverse (A_f), as well as an increase in the temperature of the end of forward (M_f) and the beginning of reverse A_s. As a result of the impact of multiple martensitic transformations and subsequent low-temperature annealing in the structure after 250 cycles in the UFG state, precipitation of Ti_3Ni_4 particles is observed during subsequent aging.

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The study was supported by a grant from the Russian Science Foundation (project no. 22-73-00289).

APPLICATION OF HYDROGEN BOND PROPENSITY CALCULATIONS TO PREDICT THERMODYNAMIC PARAMETERS OF COCRYSTAL FORMATION

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The formation of new intermolecular hydrogen bonds is the driving force of the cocrystallization process and also determines the stability of the cocrystals. [1]. Therefore, we hypothesized that the set and number of hydrogen bonds in the cocrystals can correlate with the thermodynamic parameters of the formation of these cocrystals. Hydrogen-bond propensity (HBP) method is commonly used for screening new cocrystals [2]. The principle of the HBP method is to evaluate the predominant hetero- or homomeric interactions in a two-component mixture [3]. For a long time, the Multicomponent score value (ΔHBP) calculate based on subtracting only the propensity value of the «best» homo-interaction, from the equivalent value of the «best» hetero-interaction. However, it has recently been shown that hydrogen-bond propensity calculations predict well not only the best homo- or hetero-interactions, but also hydrogen bonds for all donors and acceptors in the cocrystal [4]. Therefore, we proposed an integrated hydrogen-bond propensity calculation method for cocrystal screening, which considers all the competitive probabilities of hydrogen bonding. Details of integrated hydrogen-bond propensity calculation are presented in our previous work [10.3390/cryst13071022].

The applicability of the hydrogen-bond propensity method as an approach for predicting the thermodynamic parameters of cocrystal formation has been tested for cocrystals with stoichiometric composition 1:1 and known formation thermodynamic parameters. Thirty-seven cocrystals with a set of 40 different functional groups were analyzed. The structural diversity of the considered cocrystals suggests that the detected trends of changes in thermodynamic parameters do not depend on the structures of the components of the cocrystals, but only on their stoichiometric composition. It is shown that changes in the ΔHBP parameter correlate well with changes in enthalpy and entropy terms of cocrystal formation Gibbs energy.

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TEMPARATURE VARIATION OF THE CHEMICAL EQUILIBRIUM FOR THE ETHYL ACETATE SYNTHESIS REACTION: EXPERIMENTAL DATA, THEMODYNAMIC ANALYSIS AND CALCULATIONS

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So far, the esterification reaction has been widely used for synthesis of many esters either in a laboratory or for industrial purposes. Coupling of the chemical reaction with the purification process is a promising way for increasing the total efficiency of the corresponding industrial process in terms of energy and resource costs. At the same time, successful design of such a coupled process is impossible to be imagined without precise data on thermodynamic properties of mixtures used.

A significant amount of data on thermodynamic properties of the acetic acid – ethanol – ethyl acetate – water system has been obtained in our research group [1,2] and the critical analysis of literature data has been performed [3]. However, literature information on this system remains rather limited and needs further comprehensive consideration.

In this work, we report the results of investigating esterification reaction chemical equilibrium for the ethyl acetate synthesis reaction with regard to the temperature dependence of both concertation variables (chemical equilibrium liquid and vapour composition) and thermodynamic parameters (chemical equilibrium constant and caloric properties).

Chemical equilibrium compositions were investigated in temperature range 293.15 K – 333.15 K. Vapour-liquid equilibria (VLE) were studied by means of dynamic method. Dynamic flow type still was applied to measure equilibrium vapour pressure at observed temperatures. Compositions of both liquid and vapour phases were determined with gas chromatography (GC) method.

Based on the experimental VLE data obtained, the activity coefficients of the components in the liquid phase were calculated. The vapour of ethanol, ethyl acetate and water were considered to behave like ideal gases. The non-ideal behavior of acetic acid vapour was described by taking into account the dimerization of acetic acid in the vapour phase.

Calculated activity coefficients values were used to estimate chemical equilibrium constant at observed temperatures and, consequently, Gibbs energy of the esterification reaction. The Gibbs-Helmholtz equation was applied for evaluating enthalpy of the esterification reaction. Entropy was calculated from the temperature dependence of the Gibbs energy.

Experimental VLE information was compared with the calculation by the UNIFAC group model. Quantum chemical calculation were used to estimate the chemical equilibrium constant, as well. The calculated value was compared with the experimental one.

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UNRAVELING THE INFLUENCE OF SURFACE MORPHOLOGY ON PHYSICOCHEMICAL PHENOMENA IN CONFINED FLUIDS: FROM LENNARD-JONES MIXTURES TO ELECTROLYTE SOLUTIONS

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Understanding the intricate interplay between surface morphology and physicochemical phenomena in confined fluids is crucial in various scientific domains, particularly in chemical thermodynamics, electrochemistry, and physical chemistry. In this presentation, we delve into the nuanced effects of surface morphology on the behavior of heterogeneous surfaces, spanning from simple Lennard-Jones mixtures to complex electrolyte solutions. Through a combination of theoretical frameworks and experimental insights, we explore how surface features such as roughness, patterning, and charge distribution profoundly impact fluid behavior and phase transitions within confined environments. Our investigation unveils the role of surface morphology in modulating interfacial tension, adsorption kinetics, and the formation of interfacial structures.

Furthermore, we scrutinize the evolution of theoretical models aimed at incorporating surface morphology effects on a molecular scale within the realm of statistical fluid physics. From rudimentary lattice models of adsorption to sophisticated theories grounded in classical molecular density functional theory, we traverse the historical landscape of model development, elucidating pivotal advancements and persistent challenges. Delving into the influence of roughness and surface patterning across diverse physical systems, we scrutinize the nexus between surface morphology and physicochemical processes. Through systematic analysis, we pinpoint scenarios where surface effects are maximized, discerning the profound impact of surface morphology on material properties and fluid dynamics.

Moreover, we shed light on contemporary research frontiers and avenues for future theoretical and computational developments. By critically examining the blind spots inherent in existing models, we delineate promising directions for advancing our understanding of complex interfacial phenomena. This comprehensive exploration, tailored for scientists and specialists in chemical thermodynamics, electrochemistry, and physical chemistry, fosters dialogue and innovation at the intersection of surface science and fluid dynamics.

EXPERIMENTAL STUDY AND MOLECULAR DYNAMICS SIMULATION OF PHYSICO-CHEMICAL PROPERTIES OF GLASSES IN THE CaO-MgO-Al_2O_3-TiO_2 SYSTEM

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The range of applications for multicomponent oxide glasses and liquids is incredibly diverse: from their use as a material to immobilize radioactive waste and in the cement industry to geology, planetary science, and long-term information storage systems. Using glasses in industry requires to have comprehensive knowledge of their properties: structural, dynamic, thermodynamic, chemical stability with respect to interaction with other materials and components of the atmosphere, stability with respect to their crystalline counterparts, etc. Unfortunately, this information is often lacking in the literature. At the same time, obtaining fundamental knowledge about the properties of glasses can help to understand the details of the internal structure of the glassy state and, based on this, predict their various properties of glasses, and select their optimal chemical composition to solve specific applied problems.

The aim of this work is to investigate the physico-chemical properties of glasses in the CaO-MgO-Al_2O_3-TiO_2 system and its subsystems. This system is e.g. important in metallurgical slags to produce novel Ti-bearing steels and in new building materials such as blended cements. The work consisted of key experiments and classical molecular dynamics simulations. The first one was divided into glass synthesis and investigation of the physico-chemical properties. Synthesis of glasses were carried out by the classical quenching method using a platinum/gold crucible in air.

The heat capacities of studied glasses were measured by two precise techniques: low-temperature (10-360 K) adiabatic calorimetry and high-temperature (300-850 K) differential scanning calorimetry. The temperature intervals were overlapped to verify the obtained results. High-temperature drop-solution calorimetry was used to investigate the enthalpy of dissolution and formation of the studied glasses. The density of solid glasses was measured using the Archimedes method, by immersion in toluene. Viscosity measurements of solid glasses and differential scanning calorimetry (glass transition temperature) were used to determine the dynamical properties.

In addition to the experimental part of the work, classical molecular dynamics simulations (MD) were conducted for all glass compositions. New pair interaction parameters for pure MgO were merged with literature data for the CaO-Al_2O_3-TiO_2 ternary system, and the calculated properties obtained by MD (density, heat capacity) were compared with the experimental values. Correct dependencies of glass properties were found when adding MgO or TiO_2 to glasses in the CaO-Al_2O_3 system, however, the absolute values differ from the obtained experimental data.

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A COMBINED APPROACH INCLUDING QUANTUM-CHEMICAL CALCULATIONS AND THE GROUP CONTRIBUTION METHOD FOR PREDICTING THE ENTHALPY OF FORMATION OF ORGANIC COMPOUNDS

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Carrying out thermodynamic analysis of reactions makes it possible to assess the feasibility of the reaction, determine the maximum degree of conversion of the reagents, the depth of the reaction and the yield of the desired products. This analysis also helps to know the temperature at which the reaction occurs and investigate the formation of by-products, which allows one to evaluate the theoretical selectivity of the process and, as a result, the quality of the final products.

When conducting thermodynamic analysis, it is necessary to use reliable data on the properties of all components of the reaction system. Therefore, obtaining reliable thermodynamic data is one of the main tasks.

With the development of experimental techniques and computational chemistry in recent years, significant progress has been made in the formation of a reliable thermodynamic data base for a large number of substances. However, there remain many compounds for which reliable thermodynamic data are either lacking or erroneous. Since the experimental measurement of thermochemical data is often a complex and expensive process, the theoretical approach still remains relevant. Conventionally, it can be divided into two main types: group additivity methods and quantum chemical methods. Deospite their empirical basis, group additivity methods retain their efficiency and sufficient accuracy in estimating the thermodynamic parameters of chemical compounds, even at the current level of computing power. Benson's additive group contribution method is especially convenient and effective for simple compounds, taking into account the appropriate parameters and the possibility of neglecting deformations and other intramolecular interactions or adequately accounting for them using additional corrections. This means that Benson's method often encounters difficulties when working with multifunctional, aromatic, or polycyclic molecules.

This work proposes a new approach combining quantum chemical modeling and the group contribution method, which allows us to take into account additional non-additive effects and interactions. This method uses quantum chemical calculations to determine additional parameters, similar to Benson's basic parameters for the additive part of the enthalpy of formation of compounds.

The developed approach was tested on various classes of compounds, including alkanes, cycloalkanes, alcohols, ketones and aromatic hydrocarbons. The average absolute deviation for all analyzed substances does not exceed 1.8 kJ/mol, which indicates the high accuracy of the proposed method.

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MACHINE LEARNING FOR THERMAL STABILITY PREDICTION OF ORGANIC COMPOUNDS

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Thermal stability is an important property for compounds. Recommended procedures for assessment of this property involve thermal analysis experiments with the following thermokinetic modeling[1]. However, in the course of screening of newly synthesized molecules and/or when rapid estimation of thermal stability is needed, the characteristic temperature (e.g., the extrapolated onset of the decomposition exotherm) is frequently used. In presentation first results on the QSPR problem, the “decomposition onset” prediction directly from the structure of compound (SMILES), will be summarized. The dataset comprising >1000 molecules has been compiled over the years by the author’s group using traditional thermal analysis tools and advanced techniques (e.g., pressure DSC[2]). Various machine learning approaches are compared and some implications for design of thermostable organic species are formulated.

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THERMODYNAMIC STUDY OF SOME REPRESENTATIVES OF THE SYNTHETIC GLUCOCORTICOIDS

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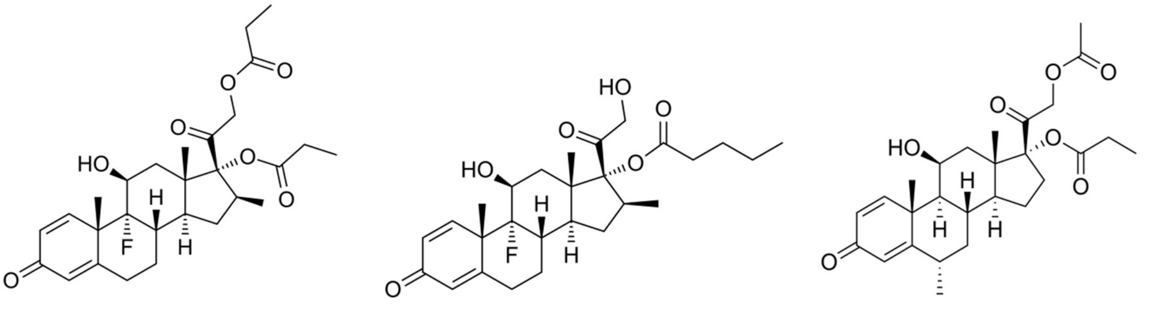
Glucocorticoids are physiologically active substances that are widely used in modern clinical practice due to the anti-inflammatory, immunosuppressive, and antiallergic properties. A special attention is focused on the natural glucocorticoids (cortisone, hydrocortisone, *etc.*) and its synthetic analogues (prednisone, methylprednisolone, dexamethasone, betamethasone, *etc.*).

The temperature dependences of the heat capacities of the synthetic glucocorticoid hormones, namely betamethasone dipropionate (**I**), betamethasone valerate (**II**) and methylprednisolone aceponate (**III**) (Figure 1) were determined for the first time using a precise adiabatic calorimetry and differential scanning calorimetry in the range of 6–500 K. The thermal stability of these glucocorticoids was also studied by thermal analysis methods; the features of thermal decomposition of the above compounds were established taking into account its functionality.



(**I**) (**II**) (**III**)

Figure 1. The structural formulas of betamethasone dipropionate (**I**), betamethasone valerate (**II**) and methylprednisolone aceponate (**III**)

The standard thermodynamic functions $[C_p^\circ(T), H^\circ(T)-H^\circ(0), S^\circ(T), G^\circ(T)-H^\circ(0)]$ of the studied compounds (**I**)–(**III**) were calculated for the range from $T \to 0$ to 500 K. The low-temperature heat capacities (20–50 K) of glucocorticoids were analyzed on the basis of the multifractal heat capacity model. A comparative analysis of thermodynamic characteristics of the synthetic glucocorticoids (**I**)–(**III**) was carried out taking into account the available literature data. Some dependences of change in the properties of compounds on the nature of the functional substituents were established.

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A CALORIMETRIC STUDY OF THE PHASE TRANSFORMATIONS IN THE FUNCTIONAL COMPOUNDS

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The information on thermodynamic properties of chemical compounds and materials allows to determine the best options for the processes involving them. The introduction of new materials into various fields of science and technology requires the study of the physico-chemical properties of compounds to optimize their production processes and further rational applications.

Precise calorimetry is a powerful tool for studying the fundamental physico-chemical characteristics (the heat capacity, the enthalpy, the entropy, the Gibbs function) of substances and materials. The most important aspect of this study is the determination of thermodynamic characteristics of the phase transformations of various functional compounds. In this work, the phase transitions of redox-isomeric complexes of transition metals, organosilicon and liquid crystalline (LC) dendrimers with different nature of the inner sphere and the outer layer, active pharmaceutical substances and organo-inorganic perovskite-like compounds were studied in a wide temperature range (6–650 K). This comprehensive study was jointly performed with the leading research teams of the Institutes of the Russian Academy of Sciences, JSC AKRIKHIN (Moscow Region), and the Sapienza University of Rome, *etc.*

Using a low-temperature adiabatic calorimetry, the temperature dependences of the heat capacities of dendrimers were studied; thermodynamic characteristics of the glass transition and the glassy state were determined; the values of the configuration and the residual entropies were estimated; the physico-chemical interpretation of the above properties was carried out taking into account the composition and structure of dendrimers. The structural effects in dendrimers were revealed: a low-temperature anomaly caused by the subtle vibrations of fragments of the inner sphere and the surface layer of macromolecules (G1–G4), as well as a high-temperature relaxation transition («nanoscale effect») for G5–G6 dendrimers; thermodynamic properties of these transformations were determined and analyzed for several representatives of dendrimers with different nature of the inner sphere and the outer layer. The revealed effects open up new possibilities for potential applications of dendrimers in biomedicine (targeted drug delivery) and nanocatalysis.

The polymorphic transitions were identified for the studied pharmaceutical substances and organo-inorganic perovskite-like compounds in the crystalline state; the corresponding thermodynamic characteristics were determined and analyzed. In the case of some compounds, thermodynamically metastable (supercooled) states were obtained; the relative thermodynamic stability of polymorphic forms under given conditions was estimated.

Thermodynamic datasets were determined for all the studied functional compounds. These fundamental values are necessary for modeling various processes involving promising materials as well as for constructing phase diagrams.

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (FSWR-2023-0025) and the scholarship of the President of the Russian Federation for young scientists and postgraduate students (SP-1369.2022.4).

A CALORIMETRIC STUDY OF COMPOSITES BASED ON MACROMOLECULES WITH NANOPARTICLES

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One of the promising and rapidly developing areas of modern chemistry is the production and research of composites. Composites are an artificially created heterogeneous solid material consisting of two or more components. Polymeric nanocomposites are currently considered as the potential candidates for the development of new materials with unique physico-chemical properties.

Despite the variety of the known nanocomposites, there are few data devoted to the study of their thermodynamic properties over a wide temperature range. In this work, the heat capacities and the enthalpies of physical transformations of polyphenylquinoxaline (PFH) and its composites based on iron(III) oxide and zinc oxide nanoparticles, as well as compositions based on a third generation polypyridylphenylene dendron decorated with dodecyl groups along the periphery, and CdS nanoparticles were studied using the methods of precise calorimetry in the temperature range 5–(480–600) K. The standard thermodynamic functions [$C_p°(T)$, $H°(T)−H°(0)$, $S°(T)$, $G°(T)−H°(0)$] of the studied composites were calculated for the range from $T \rightarrow 0$ to 600 K based on the experimental data. The experimental values of the low-temperature heat capacity were analyzed on the basis of the Debye theory of the heat capacity of solids and its multifractal model. Thermodynamic properties of composites with additive mixtures of their constituent compounds were compared. Figure 1 shows the temperature dependence of the heat capacity of the «G3 dendron + CdS» composition, as well as the additive heat capacity of its components.

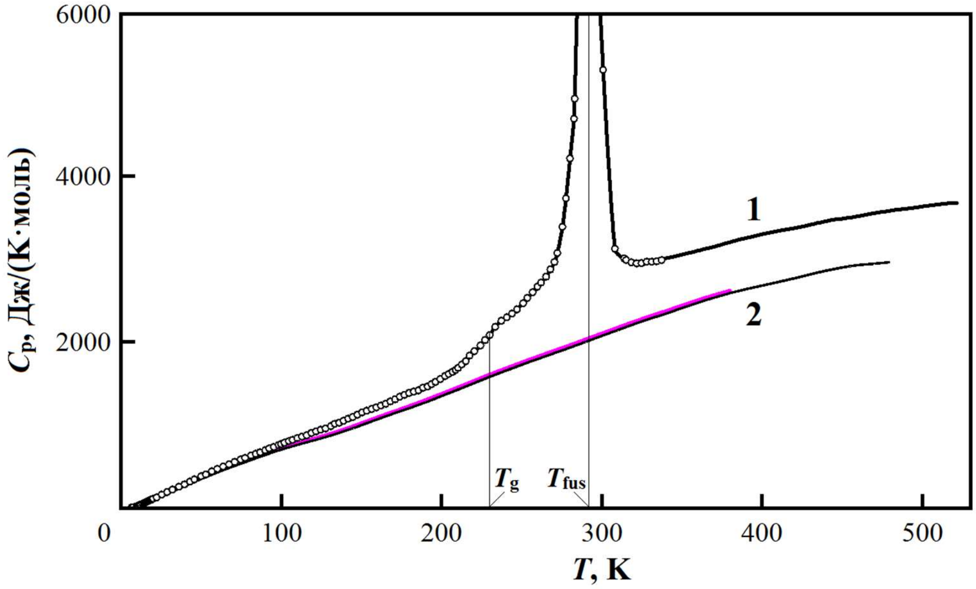

Figure 1. The heat capacities: **1** – «G3 dendron + CdS» nanocomposition; **2** – mechanical mixture «G3 dendron (34%) + CdS (66%)»; T_g – the glass transition temperature; T_{fus} – the fusion temperature

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (FSWR-2023-0024).

METHOD FOR PREPARING METASTABLE FORMS OF DRUGS

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Detection of all possible polymorphs of a pharmaceutically active ingredient is an urgent task in pharmaceutics. Among the polymorphs, metastable polymorphs are of particular interest, as they exhibit greater biological activity and bioavailability due to improved solubility compared to thermodynamically stable forms [1]. Reproducible preparation of metastable forms requires the use of more complex procedures to avoid the problem of "vanishing polymorphs". Methods used in equilibrium systems, such as saturation of solid samples of target compounds or their solvates with solvent vapour, can be used to overcome this problem [2].

Using solid-phase treatment of phenylbutazone and capecitabine with solvents vapors, a method for screening metastable forms of drugs has been developed. The model compounds studied in this work, capecitabine and phenylbutazone, are active pharmaceutical ingredients (APIs) of anticancer and anti-inflammatory drugs, respectively. The obtained results are of interest to the pharmaceutical industry, particularly in the screening of polymorphs and the production of metastable forms of pharmaceutically active compounds.

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BINOMIAL UNCERTAINTY IN MOLECULAR DYNAMICS-BASED REACTIONS ANALYSIS

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Molecular Dynamics-based reaction analysis is an indispensable tool for studying processes defying the transition-state theory (TST), where the products ratios do not follow energies of transition states. The main class of such processes are ambimodal reactions, which have a post-transition state bifurcation, so that several products form via a single transition state. Multiple runs of molecular dynamics allow to sample the space of possibilities and ultimately predict the product ratio without relying on TST, however no techniques for estimating reliability of the prediction were proposed so far. Here we show that dynamics runs follow the same rules as dies rolls, which paves a simple way for estimating their uncertainty and, accordingly, the number of runs required to achieve the required accuracy. Remarkably, we find that the majority of such studies carried out in the last 5 years use far too less runs, so that the product ratios predicted in them can be off by >50% in more than 50% of cases (Figure 1).

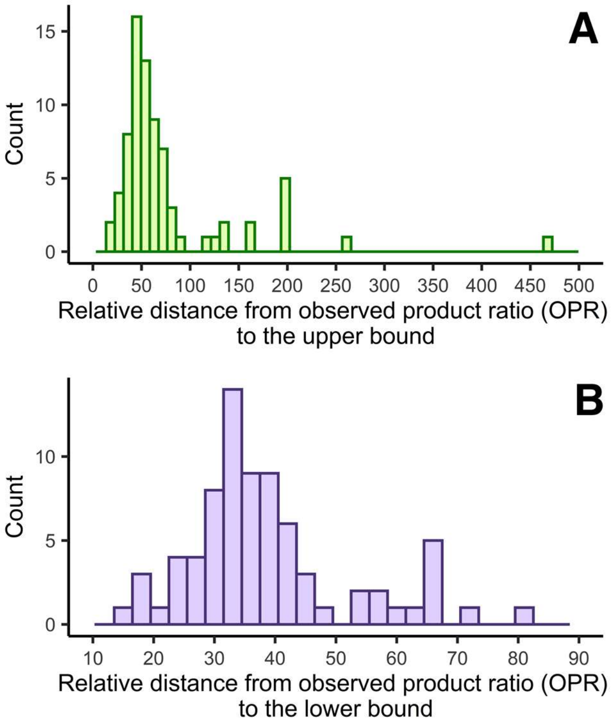

Figure 1. Distributions of relative distances from OPR to upper (A) and lower (B) bounds for 77 analyzed two-products reactions.

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EXTRANEOUS INTERACTIONS IN HIGH-TEMPERATURE MASS SPECTROMETRY STUDIES OF METAL OXIDES

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Extraneous interactions are a common problem in high-temperature research due to the increased reactivity of substances at high temperatures. A substance under investigation can react with its environment (holders, containers, cells) by different ways and these interactions negatively affect measurement results and lead to erroneous interpretation of experimental data. Such interactions may or may not be redox, and may occur by contact of solids or by mass transfer through the gas phase. Hence Knudsen effusion mass spectrometry allow one to control the qualitative and quantitative vapor composition during an effusion experiment, the method is very sensitive and informative for detection and estimation of extraneous interactions in an effusion cell.

At high temperatures (>1000 K), the variety of sample holder materials is limited, and the higher the temperature, the smaller the choice. In practice, it turns out that it is impossible to select a completely inert material. As a result, a practical requirement for container material is minimal interaction with the test substance. The availability of the material and the ease of its processing should also be mentioned as selection factors. The initial consideration of the potential holder material is carried out from the point of view of thermodynamics, and implies consideration of the corresponding phase diagrams, Ellingham diagrams, as well as, if necessary, thermodynamic assessments of the occurrence of possible side reactions. However, in fact, the possibility of using a particular material in each specific case is determined by the kinetics of extraneous interactions. This means that the proof of the material's usability is definitively confirmed experimentally. Consequently, the main study should necessarily be preceded by separate control experiments dedicated to establishing the presence of extraneous interactions, assessing their depth, and finding a way to eliminate or take them into account.

Examples from our work can be cited to illustrate the above. Contrary to the established opinion about the inertness of platinum (and platinum metals), it was found that in a non-oxidizing atmosphere at high temperatures, platinum actively dissolves the metal from oxides through the gas phase if vaporization of the oxide occurs to form a gaseous metal. As a result of this interaction, solid solutions and intermetallic compounds are formed [1]. The other case of using fused silica as effusion cells material for vaporization of ZnO or In_2O_3 [2, 3] demonstrates prevalence of kinetic factors. Despite the existence of thermodynamically stable zinc and indium silicates, it is possible to use quartz effusion cells due to the very low rate of silicate formation on the oxide-glass contact surface.

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ADIABATIC CALORIMETRIC STUDY OF PHASE BEHAVIOR OF A BINARY METHANE–PENTANE MIXTURE WITH AN EQUAL WEIGHT FRACTION OF COMPONENTS

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Digitalization of the processes of production and processing of hydrocarbon raw materials requires the development of reliable mathematical methods for modeling the phase behavior of multicomponent hydrocarbon mixtures. These methods are largely based on the results of experimental studies of binary mixtures of hydrocarbons. However, often experimental data are clearly insufficient, or they are not confirmed by independent studies. This fully applies to the most important hydrocarbon mixture methane-pentane (C1C5). In particular, with a high pentane content (more than 62 wt.%), this mixture was studied only in one work [1] with four different proportions of components using the classical PVT method. The results for equal weight fraction of methane and pentane were obtained in [1] only by extrapolation.

This work presents the results of studying the phase behavior of a binary methane–pentane mixture with equal weight fraction of the components using the method of adiabatic calorimetry. The measurements were carried out on 27 isochores when the mixture was heated from the region of the two-phase state. The resulting phase diagram of the mixture in pressure–temperature variables is shown in Figure 1. The boundary curve of the mixture was determined from the breaks in the temperature dependence of pressure and jumps in the isochoric heat capacity. The position of the critical point was determined by the maximum anomalies of the isochoric temperature coefficient of pressure and the isochoric heat capacity of the mixture from the side of the two-phase state region. The found value of the mixture critical temperature (about 17 ºC) differs from that stated in [1] by about 20 degrees and by about the same amount from the results of calculations in the NIST REFPROP package and within the framework of the cubic Peng-Robinson equation of state.

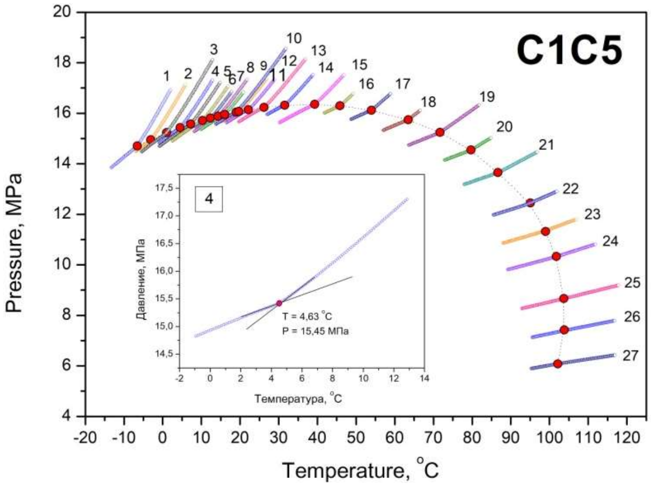

Figure 1. Phase diagram of the studied binary mixture of methane and pentane

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PREDICTION OF GAS-PHASE FORMATION ENTHALPIES USING MODERN SEMI-EMPIRICAL METHODS FOR HIGH-THOROUGHPUT SCREENING OF PROMISING ENERGETIC MATERIALS

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The enthalpy of formation (EOF) is one of the important properties for the prediction performance of energetic materials, namely, the Chaipman-Jouget pressure and velocity of detonation. The experimental EOF values in the standard (crystalline) state are usually determined by combustion calorimetry. However, this technique is cumbersome for novel energetic compounds, due to natural hindrances related to their high energy content and small amounts available. For this reason, the standard-state EOF is often estimated as a combination of the gas-phase value from quantum chemical calculations and the enthalpy of sublimation or evaporation obtained in thermoanalytical experiments [1]. Modern computational techniques allow the calculation of the gas-phase EOF for medium-size molecules containing ~ 20-30 non-hydrogen atoms with a "chemical" accuracy ~ 4 kJ/mol, at a high computational cost, though.

In the present study we focused on the benchmarking of the recently developed semi-empirical computational methodology AIQM1 [2] for the calculations of gas-phase EOF of the CHNO-containing energetic materials. To this end, we considered two datasets. The first comprises the theoretical values of the gas-phase EOF for 256 derivatives of 1,2,5-oxadiazole-2-oxide with different energetic functionalities. For the sake of comparison, we also employed an old semi-empirical approach PM3 and a highly accurate explicitly correlated W1-F12 multilevel procedure along with both atomization energy and isodesmic reaction approaches. The second benchmarking group contains the experimental EOF values of 205 CHNO compounds. To compare the gas-phase EOF with the experimental values, the former values were complemented by sublimation enthalpies estimated with the recently proposed modified Troutone equation [1]. It was found that the maximum absolute deviation for the both datasets do not exceed 105 kJ/mol, while the average absolute deviation is 20 kJ/mol. The highest deviations were observed in the case of compounds containing $C(NO_2)_3$ functionality.

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A MASS SPECTROMETRIC INVESTIGATION OF THE VAPORIZATION THERMODYNAMICS OF THE WO_3-ZnO SYSTEM

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Functional materials based on the zinc tungstate can be used in various fields of the technology, electronics and medicine. Thus, due to the scintillation properties, high sensitivity and radiation purity, single-crystal $ZnWO_4$ is a unique detector material for monitoring radiation and observing rare events. Methods for producing such materials are often associated with high temperatures, the selection and application of which requires information about the processes of vaporization in the WO_3-ZnO system.

The study [1] of vaporization processes in the WO_3-ZnO system was carried out for the first time by Knudsen effusion mass spectrometry (KEMS). Equilibrium samples of the system of phase composition [ZnO+$ZnWO_4$], [$ZnWO_4$], and [WO_3+$ZnWO_4$] were obtained by solid-phase synthesis in air at 1273 K and characterized by X-ray diffraction analysis. KEMS experiments were carried out in the temperature range 1225-1495 K using quartz effusion cell on a high-temperature magnetic mass spectrometer MS-1301. The instrument sensitivity constant was determined in each experiment by the method of the complete isothermal evaporation [2].

The saturated vapor over the pure ZnO is represented by Zn and O_2 species. The partial pressure of oxygen was not measured experimentally due to the design features of the instrument. The partial pressure O_2 was calculated by the condition of congruent sublimation. The vapor over WO_3 is represented by species W_2O_6, W_3O_8, W_3O_9, and W_4O_{12}. On the basis of work [3] performed earlier, interpretation of the obtained mass spectrum of the gas phase over WO_3 was carried out.

Only ZnO sublimation products were detected over the [ZnO+$ZnWO_4$] region in the temperature range 1330-1430 K. The main species of the gas phase over the [$ZnWO_4$] and [WO_3+$ZnWO_4$] system samples are Zn, O_2, W_2O_6, W_3O_8, W_3O_9 and W_4O_{12}. The study of the temperature dependences of the partial pressures of the vapor components over all areas of the system made it possible to determine the change in the composition of the gas phase as a function of temperature and phase composition. It was established that the $ZnWO_4$(s) sublimes incongruently and saturated vapor over subsolidus region the WO_3-ZnO system is enriched in ZnO sublimation products. As a result of vaporization study of the melt, possible existence of a homogeneous azeotrope with the composition of 49.8 ± 2.4 mol.% ZnO at 1515 K was assumed.

Partial pressures made it possible to determine the activities of the components of the condensed phase and to calculate the standard enthalpies of heterogeneous and gas-phase reactions. The standard enthalpies of formation of the gaseous oxides W_2O_6, W_3O_8, W_3O_9 and W_4O_{12} and the $ZnWO_4$(s) were found. The obtained value $\Delta_fH°_{298}$ ($ZnWO_4$) = $- 1235.1 \pm 31.8$ kJ/mol is in agreement with the literature data determined calorimetrically [4].

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POLYMORPHISM IN MULTICOMPONENT CRYSTALS OF RILUZOLE WITH HYDROXYBENZOIC ACIDS

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In this work, we investigate the influence of positional isomerism on the packing arrangements and the network of hydrogen bonds in multicomponent crystals of the drug riluzole [1] with hydroxyl derivatives of benzoic acid. A combined theoretical and experimental approach using virtual screening, X-ray diffraction, thermal analysis and periodic DFT computations was conducted to highlight the critical significance of the mutual arrangement of OH groups in the packing of these multicomponent crystals, ionization state of the components and the aptness to form multiple crystal forms.

From the performed survey of multicomponent crystals of RLZ deposited in the Cambridge Structural Database, we found that salicylic acid derivatives with $pKa < 3.8$ form salts with riluzole, while benzoic acid derivatives not containing hydroxyl groups in ortho position form cocrystals. A number of multicomponent crystals of riluzole with salicylic, 4-hydroxybenzoic, 2,3-, 2,4- and 2,6-dihydroxybenzoic acid were obtained and structurally characterized. Variation of experimental conditions allowed us to isolate the samples of metastable polymorphic forms of the salts with salicylic, 2,4- and 2,6-dihydroxybenzoic acids. For the RLZ + 2,6-dihydroxybenzoic acid salt Form II, the crystal structure was solved from powder diffraction data of high-energy synchrotron radiation. The hydrogen bond network was found to be identical in Form I and Form II, and the difference was mutual orientation of hydrogen-bonded layers, which is an example of rare packing polymorphism phenomenon. The metastable form was found to undergo an irreversible phase transition at about 120°C accompanied by exothermal event on the DSC thermogram. For salicylic acid salt, two polymorphic modifications were discovered in addition to the form known in the literature [2], and stability relationship between them was studied based on DSC, hot stage microscopy and dissolution studies. In addition, solvated salt forms were found in the systems with 2,4- and 2,6-dihydroxybenzoic acids when water, dioxane and DMSO were used as solvents during salt preparation.

For the obtained phases and pure components, the dissolution parameters were determined in aqueous buffer solutions and organic solvents, and salt formation enthalpies and free energies were determined from the thermodynamic cycle.

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The work was supported by Russian Science Foundation (project no. 22-13-00031).

ANALYSIS OF THE PHASE BEHAVIOR OF A MULTICOMPONENT SYSTEM IN THE PRESENCE OF A SEPARATING AGENT

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In the industry of basic organic and petrochemical synthesis multicomponent mixtures containing biazeotropic constituents are encountered. An example could be the production of higher fatty alcohols by hydrogenation of synthetic fatty acids and their esters [1]. At one of the stages of this production, the esterification stage, due to the peculiarities of the technology used, it is not possible to obtain pure esters without impurities of carboxylic acids. Therefore, the question of the possibility of separation the resulting mixture of esters and carboxylic acids becomes relevant. Separation of biazeotropic mixtures is a complex task that requires analysis of the phase behavior of the system under study, including in the presence of a separating agent. Previously, we obtained data on separation of the butylpropionate (BP) – propionic acid (PA) – butylbutyrate (BB) – butyric acid (BA) mixture containing biazeotropic (BP-PA and BB-BA) and monoazeotropic (PA-BB) binary constituents by using sulfolane (SF) as a separating agent [2-4].

In this work, an analysis was conducted the changes in the relative volatility of the components for any composition of the separated mixture in the presence of sulfolane. In Figure 1, the arrangement of iso-manifolds of relative volatility of components is shown in concentration tetrahedrons of four-component systems. The presented images allow us to forecast the consumption of the separating agent for the effective separation of the mixtures under study.

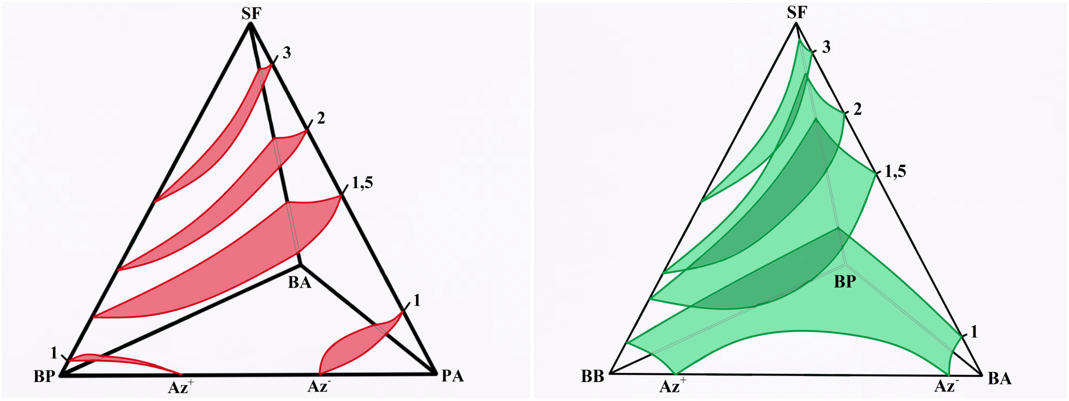

Figure 1. The iso-manifolds of relative volatility of components of biazeotropic constituents (red – BP-PA; green – BB-BA) in the presence of separating agent (SF) at a pressure of 300 mmHg. Az^+, Az^- - points of positive and negative binary azeotropes

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STUDY OF MECHANICAL PROPERTIES OF POLYMORPHIC MODIFICATIONS OF 2-PYRAZINCARBOXAMIDE USING COMPUTATIONAL METHODS

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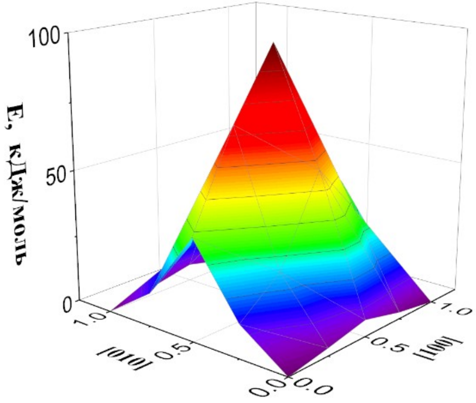
Molecular crystals of organic substances have long been considered fragile materials as a class. Close attention of researchers was paid to rare examples of crystals capable of significant plastic and elastic deformations. Now there are several dozens of examples of bending crystals which are extensively studied using experimental ant computational techniques.

The history of the systematic study of mechanically ductile organic crystals began with the discovery of systems capable of irreversible three-point bending without destruction by Ch. Malla Reddy et al. Having studied a sample of all known (at that time) bendable crystals, empirical criteria were proposed for the ability of organic crystals to undergo plastic deformation and the corresponding model [1]. The suggested model is based on the assumption of anisotropic crystal packing of layered structures, which can be (in theory) calculated using DFT and other computational methods.

In this work, we checked the compliance of the criteria and the bending model of C. Malla Reddy et al. using computational chemistry methods (MM, DFT) to simulate sliding (Fig. 1), stretching and bonding of layers using the example of crystals of α- and δ-polymorphs 2 -pyrazinecarboxamide. Energy contributions of pair-wise interactions and mechanical properties as a function of energy was studied in this work.

Based on the results of this and previous [2] research, improved criteria have been proposed for the search for new bendable organic crystals by computational methods. The work proposes a general concept for studying bendable organic crystals using computational methods with respect to thermodynamic properties of crystal structures.



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POSTER PRESENTATIONS

THERMODYNAMIC PROPERTIES OF CYTIDINE IN THE RANGE 0 – 484 K

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Cytidine is a nucleoside consisting of cytosine and ribose. It is a component of RNA and cytidine diphosphoric acids involved in various metabolic reactions in living organisms. Cytidine (and its derivatives) plays an important role in pharmacology, in particular, it is the basis for the synthesis of a promising antiviral medication against COVID-19. Reliable data on the thermodynamic properties of nucleosides are necessary to understand the energetics of biological processes involving nucleosides and expand the possibilities of their use. In this work, we present data on the thermodynamic properties (heat capacity, entropy, reduced Gibbs energy) for cytidine over the entire range of existence of the solid phase.

The cytidine ($C_9H_{13}N_3O_5$) sample was prepared by Acros Organics. Prior to the studies, sample tests were carried out to identify and confirm the declared purity using infrared absorption spectroscopy, high-performance liquid chromatography, X-ray diffraction and CHN elemental analysis. The purity of the sample was 99.6%. Using scanning calorimetry, the melting point of the substance was determined, which is in agreement with the literature data and is 484±0.5 K. No other phase transitions were detected from room temperatures to melting.

The heat capacity of the sample was measured in the range 4.2 – 300 K using two adiabatic calorimeters of different designs, described in detail earlier [1, 2]. In the first calorimeter [1], measurements were carried out in the range 4.2 – 20 K. In this case, the sample was placed in a copper calorimetric ampoule with a volume of 6 cm^3, coated with silver. The ampoule temperature was measured with a germanium resistance thermometer. In the second calorimeter [2], measurements were carried out in the range 13 – 300 K [3], and the sample was placed in a nickel ampoule with a volume of 12 cm^3. The temperature of the second ampoule was measured with a platinum resistance thermometer. The results obtained with these two calorimeters agree well (within the uncertainty of the values) with each other in the area of intersection.

Data on heat capacity above 300 K were obtained using the approach proposed in [4], which is based on dividing the experimental heat capacity into components using a model description and information on the vibrational spectrum.

The thermodynamic functions – entropy, enthalpy, and reduced Gibbs energy – were calculated in the entire solid phase region based on the heat capacity data obtained in this paper.

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EFFECT OF VANADIUM DOPING ON THE MECHANICAL PROPERTIES OF 3D-MATERIAL FROM ALLOY Al-2.3%V

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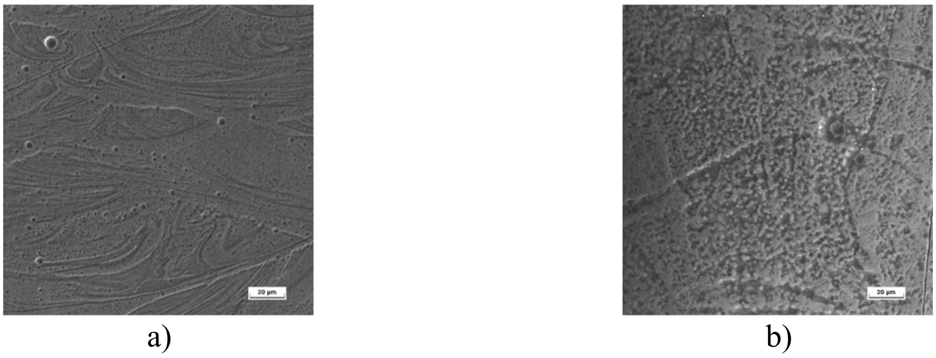
The development of new compositions of metal powders for laser printing of products using the SLS method requires not only optimization of 3D-printing modes (laser power and type, track scanning speed, preheating, atmosphere in which fusion is carried out), but also study of the influence of the composition of the feedstock on the structural features and operational characteristics of final SLS parts. Previously, we developed a method for producing vanadium-doped aluminum-based powders for 3D-printing using nitrogen melt spraying [1].

LLC "ILM&T" carried out the production of 3D-products using the SLS method from powders of Al-2.3%V alloy synthesized using the method [1] and primary Al of APK grade with the selection of optimal printing parameters on an EOS M 290 3D printer with a single-mode ytterbium fiber laser IPG YLR -400-WC. The mechanical properties of 3D-materials made of aluminum alloys were studied at the IMASH UB RAS in tensile and bending tests on an INSTRON 8801 installation.

X-ray phase analysis showed that the composition of the product produced from the Al-2.3%V alloy on a 3D-printer, in addition to Al (93%), contains Al_3V (5%), $Al_{10}V$ (1%) and Al_2O_3 (1%). In the 3D-sample Al-2.3%V (Figure 1a), due to the layer-by-layer melting of the powder, the intermetallic inclusions of the Al-V system are limited in size, and traces of laser penetration of the tracks are noticeable. In the case of a 3D-material made from primary Al (Figure 1b), only the effects of etching after polishing the section are noticeable. Both SLS materials have a homogeneous structure and porosity less than 1%.



a) b)

Figure 1. Cross-sectional sections of 3D-products made from powders:
a) alloy Al-2.3%V; b) primary Al

As a result of mechanical tensile and bending tests, a significant increase by 2 times in the strength properties of SLS products made from Al-2.3%V alloy was established while maintaining its original ductility, compared to SLS samples made from primary Al of the APK grade.

[1] RF Patent № 2754258. Method for producing aluminum-based powders for 3D printing / Shevchenko V.G., Eselevich D.A., Baklanov M.N. Publ. 28.10.2021.

The work was carried out in according with the state assignment of the Institute of Solid State Chemistry UB RAS № 124020600007-8.

QUATERNARY BIAZEOTROPY IN THE ACETONITRILE + CHCLOROFORM + CYCLOHEXENE + WATER SYSTEM

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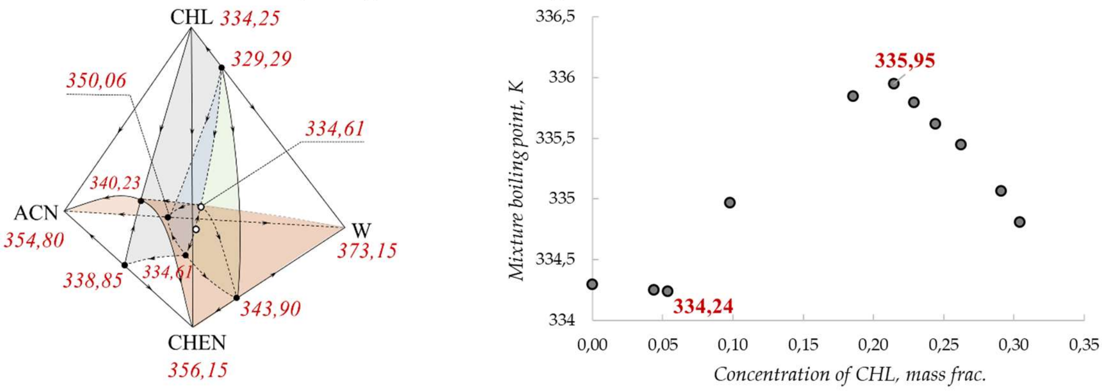
Acetonitrile (ACN), cyclohexene (CHEN), water (W) are components of a mixture for the production of cyclohexanone by direct oxidation of cyclohexene; chloroform (CHL) is a potential extracting solvent that can be used at one of the separation stages. This quaternary system is unique because two internal azeotropes were discovered and experimentally confirmed in it for the first time [1]. The maximum component of internal biazeotropy, confirmed by a full-scale experiment, before the study of this system, was three [2].

Mathematical modeling based on the local compositions equation NRTL was used at first stage of the study. The calculation showed the presence of one quaternary saddle-type azeotrope in the system (the limitation of the program used is the impossibility of displaying two azeotropes composed of the same set of components). As a result of theoretical analysis (determination of the types of singular points, Poincare indices based on data on boiling points of pure components and azeotropes - Figure 1(a), as well as solutions to the azeotropy rule), it was found that such a temperature ratio is possible only in the presence of a second internal singular point of the nodal type. In order to confirm this prediction, a full-scale experiment was conducted: ebulliometric titration of ACN + CHEN + W ternary mixture of a certain composition with chloroform (the result is shown in Figure 1(b)). It confirmed the presence of an internal singular point with temperature 334.24 K.



(a) (b)

Figure 1. Phase diagram of acetonitrile (ACN) + chloroform (CHL) + cyclohexene (CHEN) + water (W) system (a) and the dependence of the boiling point of the mixture on the concentration of CHL

Thermodynamical-topological analysis made it possible to predict the presence of a second internal singular point in the system considered and competently plan and minify a full-scale experiment in order to confirm the hypothesis.

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SOLUBILITY OF AFm PHASES AS A FUNCTION OF PAIR ENTROPY

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The hydrated ordinary Portland cement consists of various mineral phases including AFm (Aluminate Ferrite monohydrates) phases. The AFm phases are layered double hydroxides (LDH) and are represented by the following formula $Ca_2Al(OH)_6{\cdot}A{\cdot}nH_2O$, where A are anions ($OH^-$, Cl^-, I^-, NO_3^-, NO_2^-, SO_4^{2-}, CO_3^{2-}) in the interlayer space that perform a compensating function with respect to the positively charged a structural layer with $[Ca_2Al(OH)_6]^+$. The AFm phases in cements can be mineralogically and chemically quite complex, but the structure of most cement AFm phases is similar to natural mineral hydrocalumite. Amongst all cement phases, AFm plays a major role in the retention of anionic species, including radionuclides (e.g. TcO_4^-, SeO_4^{2-}). But cementitious AFm are very sensitive to relative humidity, temperature, pH and ionic strength of the pore solution in the hydrated cements and etc. The instability of the AFm phases is primarily manifested in structural phase transitions, as well as in their possible solubility. Recently Appelo showed that the solubility (log K) of various anion forms of AFm is related to the anion charge and inversely to the thickness of the anion-layer [1].

The molecular dynamic simulation approach is powerful method to study various properties of atomistic model, including thermodynamic functions. Here we use the ClayFF force field [2] for classical atomistic simulations to study structural properties and pair entropy (S_2) [3] of various cementitious AFm phases. In the ClayFF force field, partial charges of different structural oxygen atoms are assigned by taking into account, when necessary, their local coordination to the tetrahedral and/or octahedral substituting atoms in the crystal structure [2].

As a result of modeling cementitious AFm phases it was found that its solubility (log K) depend not only on the anion charge and thickness of the interlayer space, but also on the orientational relaxation and pair entropy (S_2) of H_2O molecules.

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THERMODYNAMIC PROPERTIES OF CALCIUM STANNATE PHASES FROM COMPUTER ATOMISTIC SIMULATIONS

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Calcium stannate $CaSnO_3$ is one of the most well-known stannates due to its interesting properties and potential use as a material for an anode of lithium-ion batteries, a photosensitive element in gas sensors, a phosphor with a long glow, an inorganic pigment, and an antistatic coating. Possessing basic properties of medium strength, calcium stannate has shown activity in the aldol-croton condensation of acetone and the conversion of alcohols (ethanol and isopropanol). Due to the wide possibility of practical use, much attention is paid to the development of methods for the synthesis of calcium stannate. It is noted that, depending on the synthesis method, the crystals formed have different morphology and size. The resulting samples often contain impurity phases: SnO_2, $CaSn(OH)_6$, $CaCO_3$, Ca_2SnO_4.

As a result of the synthesis of $CaSnO_3$ by calcination of $CaSn(OH)_6$, ambiguous results were obtained on crystal morphology depending on the synthesis temperature. A single wide peak on the diffractogram of the product calcined at 450 °C indicates an amorphous structure of the sample. At a temperature of 750°C the crystal sample with microcubic morphology was obtained, and the reflection indexing confirms the rhombic structure of the perovskite type. During the synthesis of $CaSnO_3$ from $CaSn(OH)_6$ by thermo-vapor method, crystals of different morphologies at different temperatures were obtained: at 300-350° lamellar crystals were obtained, and at 400 °C − isometric crystals with a perovskite structure. In order to directly synthesize calcium stannate with the perovskite structure, it is necessary to determine the thermodynamic stability region of various oxygen-containing calcium and tin compounds.

Here we use the density functional theory (DFT) to study the thermodynamic properties of atomistic models of calcium stannate: $CaSnO_3$, $CaSn(OH)_6$, $CaSn_2O_4(OH)_2$. The GTH pseudopotentials [1] were used for all atoms (Ca, Sn, O, and H) of models. The generalized gradient approximation parameterized by Perdew et al. [2] was used for the exchange-correlation terms. The thermodynamic properties (constant volume heat capacity, C_v, Helmholtz free energy, F, entropy, S) were obtained via phonon energy calculated using the harmonic approximation approach. The thermodynamic properties of the calcium stannate compound were calculated in wide range of temperatures (0-1500 K) and showed good agreement with available experimental data.

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THERMODYNAMICS OF COMPLEX FORMATION OF 1-AZA-18-CROWN-6 AND 18-CROWN-6 WITH Ag^+ IONS IN DMSO

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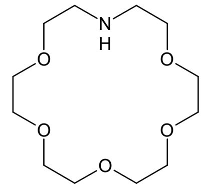
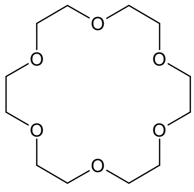
The reaction of the formation of the molecular complex of 1-Aza-18-crown-6 with silver ions (Ag^+) in dimethyl sulfoxide (DMSO, 99%) at T = 298.15 K was studied using isothermal titration calorimetry. The results were compared with the thermodynamic parameters of complexation of the silver ion with 18-crown-6 obtained early [1].



1-Aza-18-crown-6



18-crown-6

The heats of mixing of solutions of silver salts with solutions of 1-Aza-18-crown-6 in DMSO were determined using a TAM III calorimetric titration system (TA Instruments). The thermodynamic parameters of the complex formation reaction were calculated from thermochemical data by TAM Assistant software. Mathematical modelling of optimal concentration conditions for calorimetric experiments was carried out using the TAM Assistant program, taking into account the solubility limits of the reagents under study, and ensuring a molar excess of the titrant relative to the ligand for the titration result at least 2 times with the stoichiometry of complex particle 1:1. A ligand solution in DMSO with a volume of 10 ml (or 5 ml) was loaded into the TAM III cell. The initial ligand concentration in the cell was 1 mM. The initial concentration of Ag^+ in DMSO, which was loaded into the syringe, was 0.08-0.1 mol/L. The formation of the [Ag 1-Aza-18-crown-6]$^+$ complex in DMSO was established. The thermodynamic parameters of complexation of Ag^+ with 1-Aza-18-crown-6 in DMSO were calculated as $\lg K = 3.1$, $\Delta H = -14.9 \pm 1.2$ kJ/mol, $\Delta S = 10.14$ J/mol K, $\Delta G = -17.88$ kJ/mol. The comparison between thermodynamic parameters of [Ag 1-Aza-18-crown-6]$^+$ and [Ag 18-C6]$^+$ reflect the influence of the nitrogen atom in the structure of the macrocycle on its reactivity towards the silver ion. Previously for the reaction of [Ag18C6]$^+$ complex formation in DMSO follow thermodynamic parameters have been obtained: $\lg K = 0.35$, $\Delta H = -13.0 \pm 2.5$ kJ/mol, $\Delta S = -36.9$ J/mol K, $\Delta G = -1.9$ kJ/mol [1]. It should be noted that the exothermicity of both complex formations differs within the limits of the calculated error. The stability of the [Ag 18C6]$^+$ complex is lower than the stability of [Ag 1-Aza-18-crown-6]$^+$. The entropy contribution to the change in the Gibbs energy is positive in the case of [Ag 1-Aza-18-crown-6]$^+$ and does not favor the strengthening of the [Ag 18C6]$^+$ complex.

[1] T.R. Usacheva, S.F. Ledenkov, V.A. Sharnin, *J. Therm. Anal. Cal.*, 2002, 70, 209.

The study was carried out using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT grant No. 075-15-2021-671. The work was supported by the Russian Science Foundation grant No. 23-23-00526, https://rscf.ru/project/23-23-00526.

THERMODYNAMICS OF COMPLEXATION OF THIA-CROWN ETHER MODIFIED WITH 2(5*H*)-FURANONE FRAGMENT WITH NICKEL (II) AND SILVER (I) IONS IN ETHANOL

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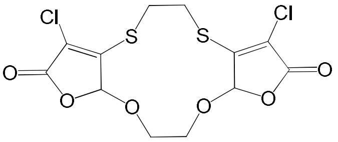
The synthesis of new substances and the study of their reactivity is one of the main tasks of experimental chemistry. Crown ethers are known as molecules that have the ability to form host-guest complexes with metal ions with high selectivity. This ability has determined the widespread use of crown ethers in the processes of selective extraction of ions, transmembrane ion transfer, catalysis, etc. Modification of the structures of crown ethers is of both scientific and practical interest with the aim of creating new materials based on them. In this work, the reactivity of thia-crown ether (M1), modified with 2(5*H*)-furanone fragments, towards nickel (II) and silver (I) ions in ethanol (94%) was studied. Compound M1 was synthesized from 5,5'-(ethane-1,2-diylbis(oxy))bis(3,4-dichloro-2(5*H*)-furanone) and ethane-1,2-dithiol under high dilution conditions in DMF in the presence of Cs_2CO_3 and isolated as an individual *dl*-diastereomer. The study was carried out by isothermal titration calorimetry (ITC) and UV spectrophotometry. Thermochemical experiments were carried out on a TAM III calorimeter equipped with a titration module and a reaction cell with a volume of 20 ml. Spectrophotometric experiments were carried out on a Shimatzu-UV 1800 spectrophotometer.



M1

It was established that under the experimental concentration conditions used, limited by the low solubility of M1 in ethanol, 1:1 complexes with nickel (II) and silver (I) cations are formed. The stability constants of the $[Ni\ M1]^{2+}$ and $[Ag\ M1]^{+}$ complexes were determined by the spectrophotometric method (lg$K$ = 3.44 ± 0.35 and lg$K$ = 3.73 ± 0.24, respectively). Mathematical processing of the spectrophotometric titration results was carried out by the KEV program [1]. From ITC data elaborated with TAM Assistant software, the following thermodynamic parameters of $[Ag\ M1]^{+}$ complexation were obtained: lg$K$ = 3.2 ± 0.3, ΔH = -7.3 ± 1.6 kJ/mol, ΔS = 36.34 J/ mol·K, ΔG = -18.2 kJ/mol. The stability constants of $[Ag\ M1]^{+}$ obtained by different methods are consistent within the calculated error. Previously, when studying the complexation of silver(I) ion with crown ether 18-crown-6, which contains only O-donor atoms in the macrocycle and has a larger cavity size, the following parameters were obtained in ethanol (94%): lg$K$ = 3.47± 0.2, ΔH= -27.4 ± 0.15 kJ/mol, ΔS = -22.5 ± 0.6 J/mol·K, ΔG = -19.8 ± 0.2kJ/mol [2]. The complexes $[Ag\ M1]^{+}$ and $[Ag\ 18K6]^{+}$ have almost the same stability in ethanol, but the exothermicity of complexation of Ag (I) with 18K6 is higher. The complex $[Ag\ M1]^{+}$ is enthalpicly and entropically stabilized. In contrary the entropic contribution to the change in the Gibbs energy of $[Ag\ 18C6]^{+}$ is negative.

[1] A.N. Meshkov, G.A. Gamov*, Talanta,* 2019, 198, 200.
[2] T.R. Usacheva, S.F. Ledenkov, V.A. Sharnin, *J. Therm. Anal. Cal.,* 2002, 70, 379.

The study was carried out using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT grant No. 075-15-2021-671. The work was supported by the Russian Science Foundation grant No. 23-23-00526 https://rscf.ru/project/23-23-00526.

PHOTOACTIVE β-DIKETONATE COMPLEXES. SYNTHESIS AND CHARACTERISATION

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β-Diketonate complexes of lanthanides were first synthesised and described by the scientists Urbain G. and Budischovsky E. in 1897 [1]. Aromatic ligands transfer energy more efficiently than aliphatic ligands due to the smaller energy gap between the triplet excited state and the emission state of the lanthanide ion. A series of complexes based on the ligand 1-(4-fluorophenyl)-3-(4-bromophenyl)-propane-1,3-dione have been synthesised, fig. 1. The structure of the obtained compounds was confirmed by a complex of physicochemical analytical methods including IR, NMR spectroscopy, mass spectrometry and chromatographic analysis. The study of the optical properties of the synthesized compounds has begun. The absolute quantum yield of fluorescence for the samples in methylene chloride solution (C = 10-6 mol/L) and in the solid state was measured using a FluoTime 300 time-resolved spectrometer (PicoQuant, Germany) with an excitation wavelength of 350 nm. The measurement was conducted with an integration sphere. Figure 2 shows the results.

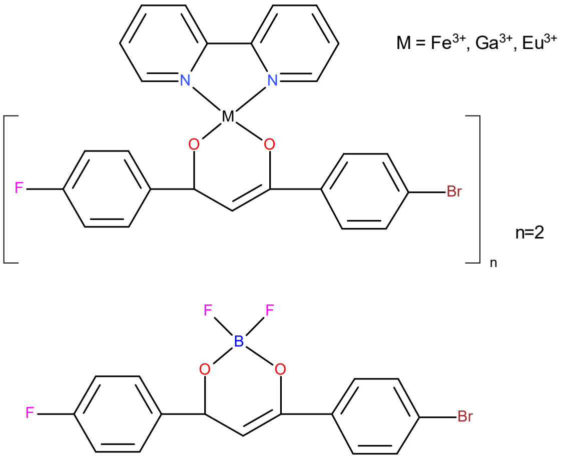

Figure 1. Scheme of β-diketonate complexes

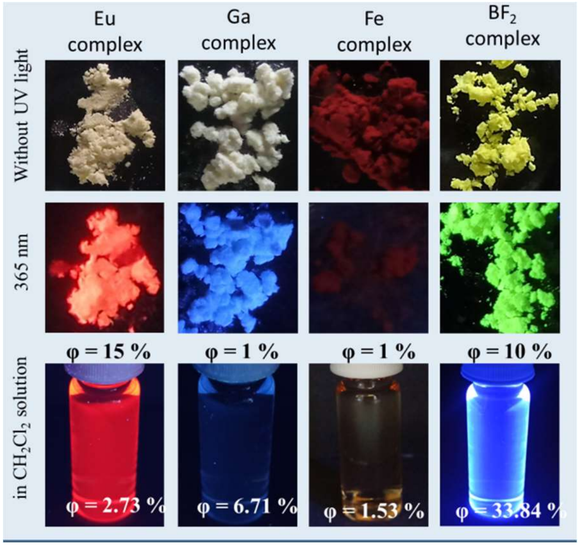

Figure 2. Optical properties and their dependence on the complexing ion's nature

Based on DSC data, the Eu complex does not exhibit any phase transition, indicating the presence of an amorphous state. The sample containing iron ions is characterised by an amorphous glassy phase with no melting point. The Ga complex undergoes melting during the heating cycle at 324°C and crystallisation during cooling (Tcr = 219°C). Additionally, all synthesised samples exhibit high-temperature stability (Tdec > 249°C). At this stage it can be concluded that the nature of the complexing ion has a significant influence on the phase behaviour of the system, temperature stability and photophysical properties.

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The financial support of Russian Science Foundation (Project number no. 23-13-00015).

PHASE BEHAVIOR FEATURES OF BINARY MIXTURES WITH PRESSURE VARYING

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Usually, when studying the structures of vapour-liquid equilibrium diagrams under changing external conditions (more often pressure), a qualitative transformation of the diagram is considered, i.e. its evolution (the appearance / disappearance of singular points through tangential azeotropes of various types – boundary / internal). At the same time, other transformations may occur in the system while maintaining the topological structure of the diagram, in particular, the degree and nature of deviation from ideal behavior may change. Such changes in the diagrams of excess Gibbs energy (coefficients of component activities) concentration dependences can have a significant impact on the localization of azeotropes in composition simplexes: expand or narrow the area of singular points existence, open additional ways of diagram evolution [1].

The paper [2] presents an analysis of vapour-liquid diagrams for binary zeotropic and azeotropic mixtures, in which the degree of deviation of the liquid phase from the ideal behavior and the nature of the deviation (transition from positive to mixed deviations) changes with the pressure change. The theoretical conclusions are confirmed by examples of real mixtures. The transformation of the activity coefficients concentration dependences at the quantitative and qualitative level affects the nature of the course of the phase equilibrium curve at different pressures (intersection points appear), which in turn affects the value of the relative volatility and, as a result, the distillation processes. An example of a isobutyl alcohol – isobutyl acetate binary mixture is indicative: the system begins to show mixed deviations from ideality with pressure increasing [2].

The authors [3] describe the evolution of complex azeotropy in the benzene – perfluorobenzene – water system and its binary constituent benzene – perfluorobenzene. The latter is interesting because the nature of the deviation (mixed) remains, but the course of activity coefficients dependence, location of pseudo-ideal points and the course of the phase equilibrium curve changes with pressure increase. In addition, the Bancroft point is realized in the system at pressures close to atmospheric (on the order of 107-110 kPa), which opens up additional ways of evolution (two binary azeotropes disappear through an internal tangential azeotrope).

[1] V.M. Raeva, L.A. Serafimov. *Theor. Found. Chem. Eng,* 2003, 37, 250.
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HYGROSCOPIC PROPERTIES AND PHASE EQUILIBRIA OF SOME DEEP EUTECTIC SOLVENTS BASED ON CHOLINE CHLORIDE

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Deep eutectic solvents (DES) are solutions of Lewis or Bronsted acids and bases with compositions close to eutectic. DES is finding more and more potential applications in chemical industry due to the combination of a number of unique properties. The main disadvantage of DES is their high hygroscopicity. Small changes in composition lead to sharp changes in their basic physicochemical properties: density, viscosity, electrical conductivity, crystallization temperatures. When using DES in technology, it is important to control all parameters of solvents. In this regard, it is necessary to have data on the range of stability of DES in relation to moisture and to know the equilibrium compositions of three-component mixtures “DES - water” under given conditions. The objects of this work were four systems based on choline chloride, which are most widespread in chemical technology along with other DES: the binary system "water - choline chloride", and three quasi-binary sections with a molar ratio of 2:1 of the first component related to second in the systems: "urea (1) - choline chloride (2) - water", "ethylene glycol (1) - choline chloride (2) - water", "glycerol (1) - choline chloride (2) - water".

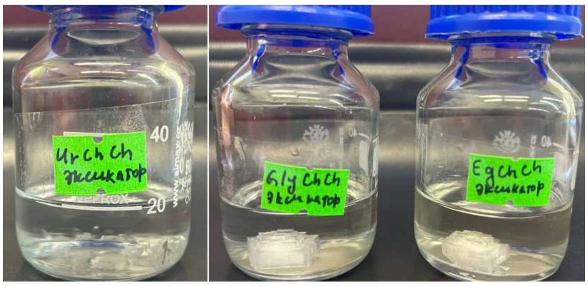

Figure 1. Crystals that obtaind by slow evaporation of water from DES solutions.

Using the isopiestic method, the hygroscopic points of DES - water solutions were determined in the relative humidity range from 4.5 to 86% at the temperature 22 ± 0.5 °C. Saturated vapor pressure of water was additionally assessed under the assumption of an ideal gas model. It was found that at low humidities, crystals were obtained in equilibrium with DES - water solutions; which contradicts the widespread information in the literature that anhydrous DES systems have eutectic temperatures below room temperature. Figure 1 shows solutions of DES with water that were subjected to slow evaporation of water in a desiccator with dried potassium hydroxide. In systems based on glycerol and ethylene glycol, crystals of choline chloride were observed, and in the system with urea, crystals were obtained that differed in geometry from choline chloride and needle-shaped urea crystals. The latter result requires further detailed study by spectral and thermal analysis methods. In the current study the compositions of saturated solutions that are in equilibrium with crystal phases at 22 ± 0.5 °C were also determined.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (State Assignment No. 075-01252-22-03 dated 26.10.2022).

HYDROGELS BASED ON SODIUM ALGINATE AND PLURONIC F127 AS DELIVERY SYSTEMS FOR NICOTINIC ACID AND NICOTINAMIDE

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As a new functional material, hydrogels are increasingly used in the pharmaceutical field because of their flexibility, high water absorption and retention, mechanical similarity to natural tissues, good biocompatibility. Natural or synthetic polymers are mainly used to prepare hydrogels. One of the most widely employed natural gelling agents is sodium alginate, gels of which are biocompatible and have good mucoadhesive properties. However, today natural polymers are gradually being replaced by synthetic ones, since gels based on them are more stable, swell better and are convenient to prepare. A promising class of synthetic gelators are pluronics – nonionic triblock copolymers composed of a central hydrophobic chain of polyoxypropylene flanked by two hydrophilic chains of polyoxyethylene.

The use of hydrogels in pharmaceuticals is based on the fact that their polymeric matrix holds drug molecules, ensuring their controlled and sustained release. This may be especially relevant for medicinal compounds that reach their maximum concentration in the bloodstream too quickly and then are also rapidly eliminated from the body. Such compounds are water-soluble vitamins, such as nicotinic acid and nicotinamide, which are applied to treat pellagra, vascular diseases and alopecia. The development of topical hydrogels with optimal, prolonged release of these biomolecules is very important task for today.

Based on this, the purpose of present work is to reveal the regularities of the influence of the structure of polymers-gelators on the release rate of nicotinic acid and nicotinamide from hydrogels. The structural and mechanical properties of the hydrogels prepared on the basis of sodium alginate and pluronic F127 were described and analyzed. The effect of nicotinic acid and nicotinamide on the gel formation and stability of the hydrogels was investigated. Using ^{1}H NMR and FTIR spectroscopy the sites of drug-polymer interaction were identified. The release kinetics of nicotinic acid and nicotinamide from the hydrogels was studied using a Franz diffusion cell. The influence of the structure of gel-forming polymers on the release of the biomolecules from the hydrogels was analyzed.

A NEW ALGORITHM FOR CALCULATING THE CONTACT ANGLE OF BINARY MIXTURES IN SLIT PORES

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Surface phenomena determine the behavior of liquids in porous media and on wetted surfaces. The correct accounting of these phenomena is the basis of accurate continuous models of fluid dynamics [1]. The contact angle is a key value that provides a quantitative characterization of surface phenomena.

Currently, there is no general theory that allows describing and predicting the behavior of binary mixtures in slit pores. The surface issue in the case of completely non-wetting liquids has already been studied [2]. In this study, a generalization of this theory for an arbitrary contact angle will be presented, which will underlie a new algorithm for determining the magnitude of the contact angle from the density profile.

To validate the theory, numerical methods (molecular dynamics) were used. Systems consisting of a mixture of n-decane and water on calcite and muscovite substrates were considered. As a result of modeling and applying the new algorithm, the following results were obtained: for a system on a calcite substrate, the contact angle is 127°, the results of 122° and 116° are given in the literature [3]; in the case of a system with a muscovite substrate, the angle is 164°, which is very well consistent with the literature – 163° [4]. These results show the correctness of the developed theory and the effectiveness of the new algorithm.

In the future, the theoretical model will also be tested on data obtained as a result of classical DFT. As a further generalization of the theory, it is planned to consider cases taking into account different phase interaction energies, taking into account the molecular structure of matter and obtaining analytical formulas for the case of a dynamic contact angle.

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[4] F. Jiménez-Ángeles, A. Firoozabadi, *The Journal of Physical Chemistry C*, 2016, 120(22), 11910–11917.

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SELF-ASSEMBLY OF BIOPARTICLES IN THE DIELECTROPHORESIS MICROFLUIDIC CHANNEL

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Among the several sorting techniques, dielectrophoresis is popular method. Dielectrophoresis (DEP) is a phenomenon in which a force is exerted on a particle when it is subjected to a non-uniform electric field. The force experienced by the particle is dependent on the particle size, particle shape, applied electric field, and dielectric properties of particle and carrier phase [1]. In this study, the trajectory of solid particle in the presence of electric field in the microfluidic channel is studied using boundary element method and point-particle approach. In this work, we explain how the boundary element method [2] and point-particle approach can be used to investigate the particle separation. Consider a small solid particle suspended in a dielectric fluid under the influence of the electric field. Figure 1 illustrates the top view of our studied microfluidic channel in the x–y plane. The considered microfluidic device consists of two inlets (for sample flow and buffer flow), two outlets and a separate region, wherein the non-uniform electric field generated by a pair of side wall electrodes arrangements. The rest channel walls are insulated. As shown in Figure 1, the triangular-shape electrodes are located on up and down walls in the straight channel.

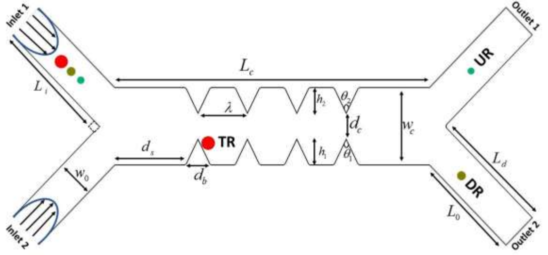

Figure 1. A top view of our proposed microchannel geometry in the x–y plane

As one can see in the Figure 2, there are three different scenarios of particle trajectories. The particle either is trapped at the straight channel or travels into up/down outlets. Figure 6 illustrates subsequent snapshots in time of the three different scenarios of particle trajectories. When the particles flow through the up or down channel outlets, it is called the up-outlet regime (UR) or down-outlet regime (DR), respectively. However, when the particles are trapped in the vicinity of electrodes, calls trapped regime (TR).

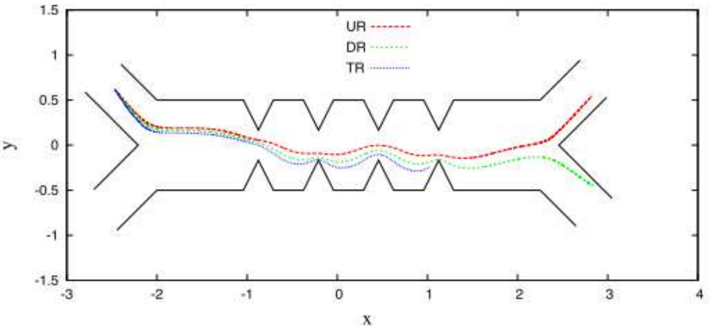

Figure 2. Particle trajectories for three different particle sorting regimes.

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THERMOCHEMICAL PROPERTIES OF SOME METHANSULFONATES OF ALKALINE METALS

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This work continues the systematic investigation of the thermodynamic properties of methanesulfonic acid's salts. It is carried out at Luginin's Thermochemistry and Chemical Thermodynamics Laboratories of Chemistry Department. The study of the properties of methanesulfonic acid's salts is of interest from a fundamental and environmental point of view. Methansulfonates are decomposed by microorganisms present in the oceans and play an important role in cloud formation and climates change. The present work is devoted to the study of the thermochemical properties of methansulfonates of lithium and potassium. There are no literature data on the enthalpies of formation of $LiSO_3CH_3$ and KSO_3CH_3.

Potassium methanesulfonate in solution was obtained by the neutralization reaction of CH_3SO_3H from equimolar amounts of KOH, which was dissolved in water and cooled in an ice bath. A solution of lithium methanesulfonate was obtained from a suspension of lithium carbonate in water by gradually adding two times the amount of CH_3SO_3H while stirring. In both cases, the resulting solutions were evaporated at a temperature 120-150°C, the mixture was cooled and filtered. Stoichiometry of Li : S or K : S and the content of impurities of other elements (< 0.1 mol. % 3d metals, phosphorus, chlorine, other alkaline, alkaline earth elements), was determined using inductively coupled plasma optical emission spectroscopy (ICP–OES Agilent 720). Additionally, the CHNS analysis method (automated analyzer CE1106) confirmed the C : H : S ratio in the obtained compounds.

The thermochemical properties of lithium and potassium methansulfonates were investigated by the method of solution calorimetry. The enthalpies of solution of $LiSO_3CH_3$ and KSO_3CH_3 were measured in water at 298.15 K in calorimeter Parr 6755 (Parr Instrument Company). The temperature rise in each run was measured by a resistance thermometer (Parr 6772). The thermometric sensitivity was $2 \cdot 10^{-4}$ K. The enthalpies of formation of $LiSO_3CH_3$ and KSO_3CH_3 at 298.15 K were calculated on the basis of the experimental data and K^+(aq), Li^+(aq) and $SO_3CH_3^-$(aq) enthalpies of formation. The results are presented in the Table. The comparison and analysis of the obtained thermochemical properties with the literature data are carried out. The enthalpy of formation of methansulfonate ion in the solid state was estimated according to the Mostafa's scheme [1].

Table. Thermochemical properties of methansulfonates at 298.15 K

Sample	$\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{298.15}$, kJ·mol^{-1}	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{298.15}$, kJ·mol^{-1}
$LiSO_3CH_3$	−7.51 ± 0.06	−956.3 ± 4.4
KSO_3CH_3	+15.27 ± 0.40	−952.7 ± 4.4

[1] A. Mostafa, J. Eakman and S. Yarbro, *Ind. Eng. Chem. Res.*, 1995, 34(12), 4577.

Investigation was supported by Program "Chemical Thermodynamics and Theoretical Material Science" (AAAA-121031300039-1) and RSF (grant № 23-13-00138). Calorimetric measurements were performed on the equipments of MSU Shared Research Equipment Center "Technologies for obtaining new nanostructured materials and their complex study" (National Project "Science" and MSU Program of Development).

THERMOCHEMICAL PROPERTIES OF $NaH_2PO_4{\cdot}2H_2O$ AND $K_2HPO_4{\cdot}3H_2O$

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The crystallohydrates NaH_2PO_4 and K_2HPO_4 can be used as heat storage materials, energy accumulation in which occurs due to phase transformations. No information about $NaH_2PO_4{\cdot}2H_2O$ and $K_2HPO_4{\cdot}3H_2O$ enthalpies of formation has been found in the literature. These data are of interest for thermodynamic modeling of processes involving hydro- and dihydrogenphosphates of potassium and sodium. The purpose of this work is to determine the enthalpies of solution of the studied substances in water by the method of solution calorimetry and calculate their enthalpies of formation.

The studied crystallohydrates were obtained by crystallization from ternary systems H_2O – NaH_2PO_4 – K_2HPO_4 due to the difficulty of obtaining single crystals from aqueous solutions of sodium and potassium phosphates. The obtained samples were dried using filter paper, removing the mother liquor, and the residue was identified by thermogravimetry (NETZSCH TG 209 F1 Libra) and X-ray diffraction analysis (Bruker D8 Quest).

The enthalpies of solution of $NaH_2PO_4{\cdot}2H_2O$ and $K_2HPO_4{\cdot}3H_2O$ were measured in water at 298.15 K in calorimeter Parr 6755 (Parr Instrument Company). The temperature rise in each run was measured by a resistance thermometer (Parr 6772). The thermometric sensitivity was $2{\cdot}10^{-4}$ K. The enthalpies of formation of the studied compounds was calculated from experimental data in three ways: 1) using the enthalpies of solution in water and the enthalpies of formation of the corresponding anhydrous salts; 2) according to the enthalpies of ion formation in an infinitely dilute aqueous solution, assuming that the dominant ionic form in the case of sodium salt is dihydrophosphate, and in the case of potassium salt is hydrophosphate; 3) taking into account acid-base equilibria arising in solutions of phosphates. In addition, the enthalpies of formation of the studied salts were estimated according to the Mostafa's scheme [1]. The results obtained are in good agreement with each other. The table shows the values of the enthalpies of formation of crystallohydrates recommended by us.

Table. Thermochemical properties of crystallohydrates at 298.15 K

Sample	$\Delta_{\text{sol}}H^{\text{o}}_{298.15}$, kJ·mol^{-1}	$\Delta_{\text{f}}H^{\text{o}}_{298.15}$, kJ·mol^{-1}
$NaH_2PO_4{\cdot}2H_2O$	19.8 ± 1.1	−2134.4 ± 1.9
$K_2HPO_4{\cdot}3H_2O$	16.4 ± 0.9	−2677.2 ± 1.8

[1] A. Mostafa, J. Eakman and S. Yarbro, *Ind. Eng. Chem. Res.*, 1995, 34(12), 4577.

Investigation was supported by Program "Chemical Thermodynamics and Theoretical Material Science" (AAAA-121031300039-1) and RSF (grant № 23-13-00138). Calorimetric measurements were performed on the equipments of MSU Shared Research Equipment Center "Technologies for obtaining new nanostructured materials and their complex study" (National Project "Science" and MSU Program of Development).

BINDING CONSTANTS OF SMALL MOLECULE DRUG LIGANDS WITH LYSOZYME AMYLOID FIBRILS

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Experimental data on the affinity of various organic substances to amyloid fibrils can help to understand the structure-activity relationships and develop the predictive models. This may facilitate the development of diagnostic agents for amyloid deposits imaging. Most of the data reported at the moment were obtained using radioligand binding assay which is unavailable to the majority of researchers.

Here we show that fluorescent competition assay can be used to obtain well-reproducible binding affinities of non-fluorescent ligands to fibrils. The plot of the ratio of thioflavin T fluorescence intensity in the absence (F_0) and in the presence (F) of a ligand against the ligand concentration ([L]) allows to determine the value of the binding constant K_L using linear regression given by the following equation:

$$\frac{F_0}{F} = 1 + \frac{[\mathrm{L}]/K_L}{1+[\mathrm{T}]/K_T} \quad (1),$$

where [T] and K_T are thioflavin T concentration and binding constant, respectively.

Binding of a series of small molecule drug ligands to the mature fibrils of lysozyme was studied. The structure–affinity relationships were considered, and molecular descriptors correlated with the binding constants were identified.

This work has been supported by the Kazan Federal University Strategic Academic Leadership Program (Priority-2030).

MANIFESTATION OF MOLECULAR INTERACTIONS BETWEEN ASPARAGINE AND PYRIDINE MONOCARBOXYLIC ACIDS IN WATER AND BUFFER SOLUTION FROM CALORIMETRIC STUDY

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Nitrogen-containing heterocyclic organic molecules as the structure fragments of many drugs, dyes and food additives have been the subjects of study by chemists, pharmacologists and physicists over the past decades to find a connection between chemical structure and biological activity. The three isomeric molecules of picolinic, nicotinic and isonicotinic acids are the pyridine derivatives (PyCOOH) and have great importance due to their chemical and biological properties. Investigation of the interactions between pyridine derivatives and model compounds of protein (amino acids, peptides) is of special interest. Studies on physicochemical properties of their aqueous solutions play key role in understanding the nature of molecular interactions in more complex liquid mixtures. L-Asparagine is one of the 20 most common natural amino acids in living organisms. It has carboxamide as the side chain's functional group. L-Asparagine (Asn) has a high propensity to hydrogen bond, since the amide group can accept two and donate two hydrogen bonds. Asparagine is an important regulator of anabolic metabolism and cancer cell proliferation.

The interactions of L-asparagine (Asn) with nicotinic acid (NA), isonicotinic acid (INA) and picolinic acid (PA) in water [1] and in aqueous buffer saline solutions were investigated by calorimetry method at 298.15 K. The obtained stability constants ($\lg K_c$) and thermodynamic parameters of complex formation ($\Delta_c G$, $\Delta_c H$, $\Delta_c S$) verified that Asn can form 1:1 complexes with the three isomeric pyridine carboxylic acids in aqueous solutions studied. The results indicate the formation of more stable complexes between Asn and PyCOOH isomers in water than in buffer. The complexation of amino acid is influenced by -COOH group position in the pyridine ring relative to the nitrogen atom. Strengthening of the stability of the Asn complexes formed in water follow the order PA<INA<NA, and their binding constants were found to be as moderate strength. In case of aqueous buffer saline solutions, the binding affinity of Asn with PyCOOH isomers follows the order as PA<NA<INA.

The complexation of Asn with PyCOOH is influenced by the *pH* of medium and ionic state of the reagents investigated. The large and positive entropic term compared to the small and negative enthalpic one displayed a predominantly entropy-driven process of complex formation of zwitterionic form of Asn with a molecular form of PyCOOH in the aqueous solutions (*pH* 5.1). In the aqueous buffer saline solutions (*pH* 7.4), the complexes between Asn existing in form of zwitterion - anion mixture and anionic form of PyCOOH are stabilized by both enthalpic and entropic contributions to the Gibbs energy.

It was shown that in the aqueous solutions the hydrogen bonds and van der Waals interactions introduced as a consequence of the hydrophilic and hydrophobic effects are the most important factors contributing to the stability of the amino acid - pyridine carboxylic acids complexes obtained. At *pH* 7.4, the main interactions in Asn/PyCOOH complexes stabilization were believed to be electrostatic forces as well as hydrogen bonding.

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CHANGES IN VOLUME PROPERTIES OF STRUCTURAL ISOMERS OF PYRIDINE CARBOXYLIC ACID UPON THEIR TRANSFER FROM BUFFER TO L-HISTIDINE BUFFER SOLUTION

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The increasing interest in the physicochemical studies of pyridine carboxylic acids (PyCOOH) and their derivatives is due mainly to their biological and pharmaceutical importance. They are members of the B-vitamin family, structure fragments of molecules of food additives, antibacterial and antiviral drugs, anti-hyperlipidemic agents in the reduction the cholesterol level, etc. Understanding the interactions between the components of proteins (amino acids, peptides) and pyridine derivative molecules is especially important because these interactions provide key functions ranging from participation in biosynthesis to drug delivery. Drug - amino acid complex may be considered as a model for gaining general fundamental insights into drug - protein binding.

In this work, the densimetry method had been used to study the intermolecular interactions of structural isomers of pyridine monocarboxylic acid (PA, NA, INA) in aqueous buffer solutions (*pH* 7.4) in the temperature range (288.15 - 313.45) K. We also studied the effect of complex formation of pyridine carboxylic acid isomers, as model of drug, with L-histidine (His), as one of the components of proteins, on their volumetric characteristics in aqueous phosphate-buffered at *pH* 7.4 in the temperature range (288.15 - 313.45) K. Buffer solution *pH* 7.4 imitates the medium of the blood plasma. The results of densimetry allow one to obtain information on the nature of solute – co-solute interactions and structural rearrangements in solution occurring upon complex formation.

Using the obtained density data, the apparent molar volumes of PyCOOH isomers, standard apparent molar volumes at infinite dilution and their derivatives with respect to temperature have been calculated for the systems studied. It was shown that the concentration dependences of the apparent molar volume of PyCOOH isomers in a buffer solution are linear. For ternary systems (PyCOOH – His – buffer), these dependences have a maximum, the position of which characterizes the 1:1 stoichiometry in the resulting His:PyCOOH complexes. It was shown, that the transfer of PyCOOH from buffer to His buffer solution is accompanied by positive volume changes. The change in volume had been interpreted as the effect of the reorganization of solvent molecules during the complexation of PyCOOH with His in solution using the model of overlapping hydration co-spheres. The effects of temperature on the volume properties were discussed on the basis of Hepler approach.

The negative second temperature derivatives of the standard apparent molar volumes of PyCOOH isomers in buffer solutions indicate that those solutes are structure-breakers. It was revealed that structure-breaking effect on the buffer solution decreases in the order PA→ NA→ INA, and the (INA – buffer) solution belongs to more structured systems studied. In case of ternary systems (PyCOOH – His – buffer), the positive values of the second derivative of the standard apparent molar volumes of PyCOOH isomers with respect to temperature at constant pressure indicate an increase in the ordering of the solvent in the environment of PyCOOH with the addition of His, which may be associated with the blocking of their polar groups due to hydrogen bonding with the amino acid. It was observed that the structure-making ability increase in the series of isomers PA→ NA→ INA upon addition of His to binary solutions (PyCOOH – buffer).

DENSITY AND REFRACTIVE INDEX IN BINARY MIXTURES OF BUTYL ACETATE WITH DIBUTYL PHTALATE AND DIOCTYL PHTALATE IN THE TEMPERATURE RANGE 288.15-308.15 K

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Dibutyl Phthalate (DBP) – C6H4(COOC4H9)2 and di-(2-ethylhexyl)-phthalate, also known as dioctyl phthalate (DOF) – C6H4(COOC8H17)2 are widely used liquid plasticizers in the production of numerous polymer materials, in particular in the processing of polyvinyl chloride, adhesives, cellulose-based film coatings. Butyl acetate (BA) also plays an important role in the polymer industry as a solvent, due to its ability to effectively dissolve a wide range of polymers and resins, while having relatively low toxicity and good evaporation.

Outcomes of this research are applied to interpret the nature and type of interactions which take place between BA and DBP. The present paper reports density and refractive index for this binary system at ambient pressure over the whole range of compositions at five different temperatures of five-degree intervals between 288.15 and 308.15 K.

From these data, excess molar volumes have been calculated. Excess molar volumes are negative over the whole concentration range and decrease with rising temperature with minimum at DBP concentration about 0.4. The negative values of excess molar volumes for all the binaries mixtures over whole composition range suggest that dipole-dipole type of interactions may be possible between these unlike molecules. In addition, in the presented work, the isobaric coefficient of thermal expansion, the apparent molar volumes and the partial molar volume for each component of the BA-DBP mixtures were determined.

In this study, we have reported a detailed investigation of the refractive indices (n_D) of BA-DBP binary mixtures. The experimental values of density and refractive index are used to calculate the molar refraction, reduced molar free volume. The deviations of refractive index, molar refractions, reduced molar free volumes have been also calculated. The applicability of nine different refractive index mixing rules is tested against the experimentally measured values. To take into account non-ideality of the system mixing rule was suggested an asymmetric mixture rule for the refractive index. According to this rule, the reduced refractive index is proportional to volume fraction φ, that is

$$\left(n_{DBP}-n_{mix}\right)/\left(n_{mix}-n_{BA}\right)=k\varphi_{BA}/\left(1-\varphi_{BA}\right),$$

(1)

where n_{DBP}, n_{BA} and n_{mix} are the refractive index of DBP, BA and mixture and k is the empirical parameter. The straight line in Fig corresponds Eq.1 with k=0.39.

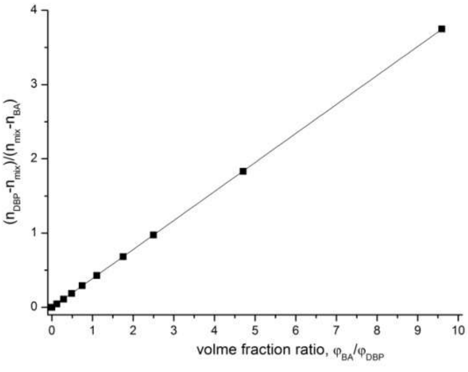

Figure. Linear dependence of the reduced refractive index on volume fraction

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THERMODYNAMIC CHARACTERISTICS OF THE ACID-BASE EQUILIBRIUM OF SOME URACIL DERIVATIVES IN WATER

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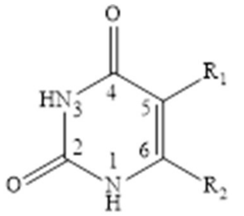
The acid-base equilibrium of biomolecules in water solutions plays one of the key roles in the vital activity of animals and plants. Most of the studies of the acid-base equilibrium of uracil derivatives in water solutions are devoted in the literature to uracil, thymine and 5-halogenuracils. Other derivatives have been studied to a lesser extent. For 5,6-substituted uracils, there is a small amount of work on the determination of dissociation constants and thermodynamic characteristics (ΔH, ΔG°, ΔS°) of acid-base equilibrium in water solutions, the reproducibility of which hasn't been evaluated or considered at all by other authors and methods.



In this work, the constants and thermodynamic characteristics of the acid-base equilibrium of 5,6-dimethyluracil, 5-(1-pentyl-4-methyl-1,2,3-triazol-4-yl)-6-methyluracil, 5-amino-6-methyluaracil, 5-cyano-6-methyluracil, 5-formyl-6-methyluracil, 6-aminouracil, 5-nitroso-6-aminouracil were determined for the first time in water solutions by the potentiometric method in the temperature range of 15–45 °C (Table).

Table. Dissociation constants and thermodynamic characteristics of uracil derivatives in water solutions (25 °C, 0.1 M KNO_3).

R_1	**R_2**	**pK_a**	**ΔG^{298}, $kJ\cdot mol^{-1}$**	**ΔH, $kJ\cdot mol^{-1}$**	**ΔS^{298}, $J\cdot mol^{-1}\cdot K^{-1}$**
H	CH_3	9.65 ± 0.03	55.0 ± 0.2	13.3 ± 0.4	-140 ± 1
CH_3	CH_3	10.26 ± 0.03	58.5 ± 0.2	11.6 ± 0.3	-158 ± 1
	CH_3	10.09 ± 0.07	57.5 ± 0.9	12.9 ± 0.4	-150 ± 2
CN	CH_3	7.00 ± 0.02	39.9 ± 0.9	12.0 ± 1.2	-93 ± 7
CHO	CH_3	7.55 ± 0.04	43.1 ± 0.2	16.3 ± 0.5	-89 ± 1
NH_2	CH_3	9.60 ± 0.03	54.8 ± 0.2	14.7 ± 0.7	-134 ± 3
H	NH_2	8.61 ± 0.06	49.1 ± 0.3	19.4 ± 0.9	-100 ± 7
NO	NH_2	5.27 ± 0.02	30.1 ± 0.1	17.0 ± 0.2	-43 ± 1

Thus, the thermodynamic characteristics of the acid-base equilibrium of 5-substituted derivatives of 6-methyl- and 6-aminouracils indicate a shift in equilibrium towards the molecular form in neutral water solutions.

THERMODYNAMIC STUDY OF THE CU-SB BINARY SYSTEM BY EMF MEASUREMENTS

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Antimony-containing intermetallic compounds demonstrate interesting thermoelectric, optical, superconductor, topological insulator, magnetic, etc. applied properties and are considered innovative functional materials of modern technology [1]. Some have recently been suggested as alternative anode electrodes to graphite in rechargeable lithium batteries, which can operate at much higher millivolts than metallic lithium and have a significantly larger volumetric capacity than graphite [2,3]. Among them, copper antimonides are also substantial base materials for application in various emerging Pb-free solders and solder-related materials systems [4].

Considering these materials' scientific and applied importance, this work aims to study the phase diagram of the Cu-Sb binary system by emf measurements. To conduct investigations, samples with selected compositions from different two-phase regions of the Cu-Sb phase diagram were synthesized by co-melting high-purity elements in vacuumed quartz ampoules. The phase compositions of prepared samples were confirmed by the powder XRD method.

To conduct thermodynamic studies, the following electrochemical cells were designed, and their emf values were measured:

$$(-)\ \mathrm{Cu}\ |\ \mathrm{Cu_4RbCl_3I_2}\ |\ \mathrm{Cu\ in\ alloy}\ \ (+)$$

The superionic conductor $Cu_4RbCl_3I_2$ served as an electrolyte, and the equilibrium crystalline alloys of the Cu-Sb system served as right-hand electrodes. EMF measurements were done in the temperature range of 290 – 430 K with an accuracy of ±0.1 mV using the high-resistance Keithley 2100 6 1/2 digital multimeter. The assembly of an electrochemical cell and measurements are described in detail elsewhere [5].

Based on equations of emf vs. temperature dependences, the partial molar functions of copper in certain phase domains of this system were calculated. The standard thermodynamic formation functions and the standard entropies of low-temperature (LT) modification copper antimonides were determined. It was observed that the emf values in heterogeneous phase regions are constant regardless of the total composition of suitable electrodes and sharply changes at stoichiometric composition of the LT copper antimonides.

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LIQUID-LIQUID EQUILIBRIUM OF QUATERNARY SYSTEM LACTIC ACID - N-BUTANOL - N-BUTYL LACTATE – WATER AT 298.15 K

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Lactic acid is a carboxylic oxyacid, which has a wide range of uses. This acid is used in the food, cosmetic and pharmaceutical industries. Polymers made from lactic acid and with its addition are actively are used in medicine as surgical sutures and implants, as well as in the production of biopolymers for biodegradable packaging.

The industrial production of lactic acid is mainly based on renewable sources. More than 50% of the cost of lactic acid obtained using the biotechnological method is due to the isolation. One of the promising methods for acid isolation is esterification and subsequent rectification of alkyl lactate. Besides this one of the most promising groups of new solvents is alkyl lactate compounds. In reaction system components (butanol and butyl lactate) are characterized by limited solubility. Still, the main challenges are the conditions and energy optimization of the process to be effective.

Experimental data on solubility in quaternary system lactic acid - n-butanol - n-butyl lactate – water system at 298.5 K and atmospheric pressure was found. Solubility was obtained by the “cloud-point technique” method. Data on ternary systems with butyl lactate were for the first time. The results obtained of the lactic acid - butanol - water system agree with literature data. The butyl lactate preferentially dissolves in the organic phase.

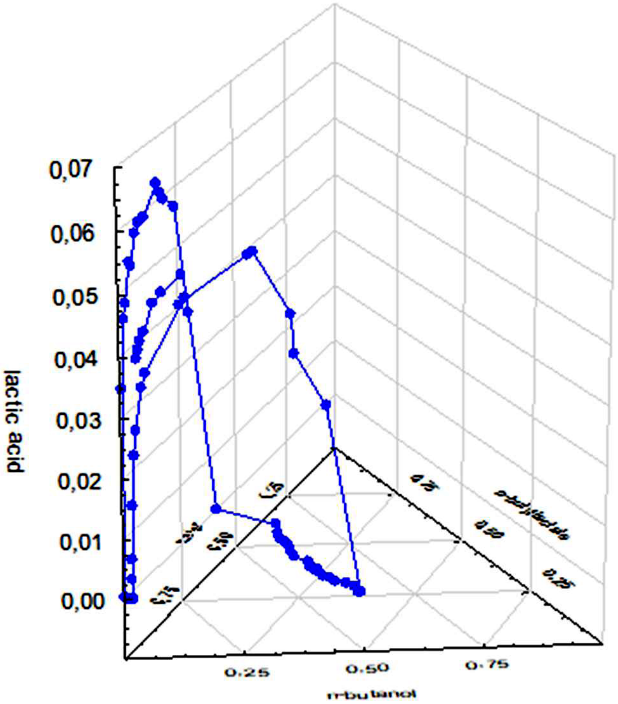

Figure 1. The diagram of LLE in the lactic acid - n-butanol - n-butyl lactate – water system at atmospheric pressure and 298.5 K (mole fraction).

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PREDICTION ENTHALPIES OF VAPORIZATION OF ESTERS OF HYDROXYCARBOXYLIC ACIDS BY QSPR METHOD

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In this work enthalpies of vaporization of alkyl glycolates, alkyl lactates and alkyl malates were calculated quantitative structure-property relationship (QSPR) method [1, 2]. We made changes to the method to reduce the error. We took into account the differences of inter- and intramolecular hydrogen bonds in liquid and in gaseous phase due to the hydroxyl group in a molecule of esters in QSPR method. The changes took into account the effect of the substituent located next to the hydroxyl group on the hydrogen bond energy. The contribution of a hydrogen bond to the total index was estimated by the equation:

$$\chi_{\mathrm{b}} = 11.3 - \left(1.316 \cdot \ln\left({}^{0-3}\chi_{\mathrm{alk1}} \cdot {}^{0-3}\chi_{\mathrm{alk2}} \cdot m\right) - 0.220\right)$$

where 11.3 is the contribution of hydrogen bond for alcohols, m is the number of carbon atoms in the molecule, 1.316 and 0.220 are parameters obtained from the regression of the experimental data, ${}^{0-3}\chi_{\mathrm{alk}}$ is total index of alkane corresponding to the substituent next to the OH group.

The final expression for the total index of esters of hydroxyl acid was obtained as:

$${}^{0-3}\chi = {}^{0}\chi + \frac{{}^{1}\chi}{2} + \frac{{}^{2}\chi}{3} + \frac{{}^{3}\chi}{4} + \chi_{\mathrm{mm}} + \chi_{\mathrm{b}}$$

where ${}^{0}\chi$, ${}^{1}\chi$, ${}^{2}\chi$, ${}^{3}\chi$ are the contributions of molecular structure; χ_{mm} is the contribution of intermolecular interaction; χ_{b} is the contribution of hydrogen bond.

The relative deviations between experimental and estimated values by the proposed QSPR method weren't exceeded 4.5% and this method can be recommended to calculated vaporization enthalpy of esters of hydroxycarboxylic acid.

Table 1. Comparison of experimental vaporization enthalpies $\Delta_{\mathrm{vap}}H^{o}(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}$ and QSPR method.

n_C	$\Delta_{\mathrm{vap}}H^{o}$ exp.	$\Delta_{\mathrm{vap}}H^{o}$ calc.	n	$\Delta_{\mathrm{vap}}H^{o}$ exp.	$\Delta_{\mathrm{vap}}H^{o}$ calc.
		alkyl glycolates			
1	52.2±1.2	49.9	5	65.0±1.1	65.5
2	55.1±1.0	53.3	6	70.7±1.3	69.5
3	58.2±1.0	57.2	8	77.6±2.1	78.5
4	62.7±1.4	61.2			
		alkyl lactates			
1	50.2±0.4	50.2	8	78.6±1.6	79.2
2	52.8±0.4	53.8	10	89.0±2.2	88.4
3	56.1±0.5	57.7	12	98.7±3.0	97.7
4	60.2±0.5	61.8	14	111.3±3.8	107.1
5	64.9±0.7	66.1	16	118.9±3.8	116.5
6	69.7±1.2	70.2			

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THERMODYNAMIC PARAMETERS OF PROTOLYTIC EQUILIBRIA FOR SOME DIPEPTIDES, AMINO ACIDS AND COMPLEXONES IN AQUEOUS SOLUTIONS

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This work presents results of investigations of acid-base interaction processes in aqueous solutions of L-valyl-L-valine, D,L-valyl-D,L-leucine, D,L-leucyl-glycine, L-leucyl-L-leucine, D,L-alanyl-D,L-leucine, L-alanyl-L-isoleucine, D,L-alanyl-glycine, D,L-alanyl-D,L-serine, L-alanyl-L-histidine, glycyl-L-histidine, β-alanyl-glycine, glycyl-glycine, glycyl-β-alanine, glycyl-L-alanine, glycyl-D,L-valine, glycyl-D,L-leucine, glycyl-D,L-serine, glycyl-D,L-threonine, L-homoserine, taurine, D-asparagine, L-glutamine, L-glutamic, glycyl-L-glutamic, glycyl-L-aspartic, N-methylimino-N,N-diacetic, ethylenediamine-N,N'-bis-(α-propionic), ethylenediamine-N,N'-bis-(β-hydroxy-α-propionic), N-(β-hydroxyethyl)-ethylenediamine-N,N',N'-triacetic, ethylenediamine-N,N'-diglutaric, ethylenediamine-N,N'-diacetic-N,N'-dipropionic, ethylenediamine-N,N,N',N'-tetrapropionic, trimethylenediamine-N,N,N',N'-tetraacetic, tetramethylenediamine-N,N,N',N'-tetraacetic, hexamethylenediamine-N,N,N',N'-tetraacetic and 2-hydroxypropylene-1,3-diamine-N,N,N',N'-tetraacetic acids.

Thermodynamic parameters ($\log K$, ΔG, ΔH, ΔS) of protolytic equilibria have been determined at 298.15 K and at ionic strength values from 0.1 to 1.5 M (KNO_3). Stepwise dissociation constants of these compounds were determined potentiometrically. The heat effects of the relevant equilibria were measured calorimetrically. The influence of "background" electrolyte concentration on the thermodynamic parameters for the protolytic equilibria investigated was under consideration. The data obtained were extrapolated to the zero ionic strength. The corresponding thermodynamic quantity values have been calculated for the standard solution ($\log K^o$, ΔG^o, ΔH^o, ΔS^o). The results have been compared with the corresponding data on related compounds (amino acids, complexones, peptides and diamines) investigated in this laboratory earlier [1-7]. A plausible explanation of changes in these quantities has been suggested in view of the aminocarboxylate structure, its set of functional groups, distance between carries of positive and negative charges, presence of hydrophobic and hydrophilic fragments, solvation features of zwitter ions). As ancillary part of this study, the spatial, electronic and energy parameters for isolated molecules and ions of some compounds were computed, and the data obtained were compared with results of structural and thermochemical investigations for the relevant dipeptides, amino acids and complexones in an aqueous solution and crystalline state.

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POLY(DIALLYLDIMETHYLAMMONIUM) CATION MOBILITY AND COUNTERION DISTRIBUTION IN WATER AND AQUEOUS SALT SOLUTION FROM MD SIMULATION AND EXPERIMENT

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Polyelectrolytes' behavior in solutions depends on interactions between the charged polymeric chain and its environment, including counterions, solvent molecules, (optionally) co-ions and other additives. Typically, a double electric layer is formed around the chain, including condensed counterions near it and a more extended diffuse "cloud" with an excess of counterions. Structural, (electro)kinetic and other characteristics of the polyelectrolyte, including properties important in practical applications, depend on its concentration as well as on the presence of additional components (e.g. a low-weight electrolyte that causes screening of electrostatic interactions). In the present work, we have studied these dependences in dilute (0.00289*m* in terms of monomer units) and semi-dilute (0.0289*m*) solutions of poly(diallyldimethylammonium) chloride (PDADMAC) in water and water+NaCl, using atomistic molecular dynamics (MD) simulation and comparing MD results with experimental data obtained both from the literature and from our own measurements.

The MD simulation has shown that adding the salt to the aqueous solution makes the polycation chain only slightly less stretched, despite significant counterion condensation, while the diffuse counterion "cloud" becomes much more compact. At the same time, the calculated polyion electrophoretic mobility decreases significantly, in comparison with a salt-free solution, already at low salt concentrations. In a more concentrated (semi-dilute) PDADMAC solution, the polycation mobility calculated by MD becomes somewhat lower (Figure 1), as the effective charge of the polycation with a "cloud" of counterions decreases due to an additional contraction of the "cloud". Our simulation results agree with the behavior of the electrophoretic mobility observed experimentally, thus providing a good complement to the experiment and suggesting probable molecular mechanisms for these effects.

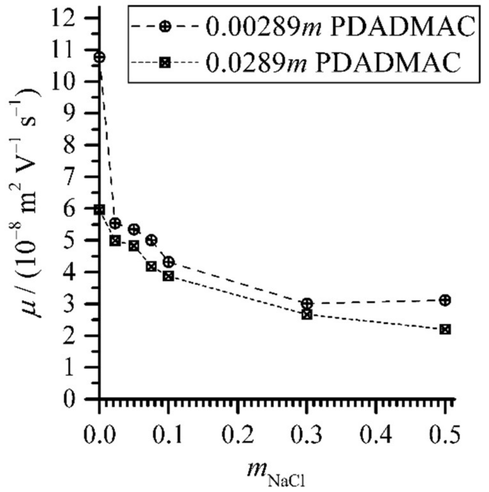

Figure 1. The electrophoretic mobility μ of poly(diallyldimethylammonium) 40-mer cations in water and NaCl aqueous solutions (m_{NaCl} is the molality) from MD simulations.

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DEEP EUTECTIC SOLVENTS DATABASE

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Today, there is an exponential increase in the number of publications devoted to the study of the properties of deep eutectic solvents (DES). According to google.scholar, the total number of scientific articles and patents is approximately 70,000, that contain phrase «deep eutectic solvent». Despite the huge amount of information on the properties of DES, there is no systematic presentation of the physicochemical properties of this type of solvent in the scientific literature. The goal of this project is to create a database that will contain information on the basic physico-chemical properties of DES with the ability to export values for their further use for both scientific and technological purposes.

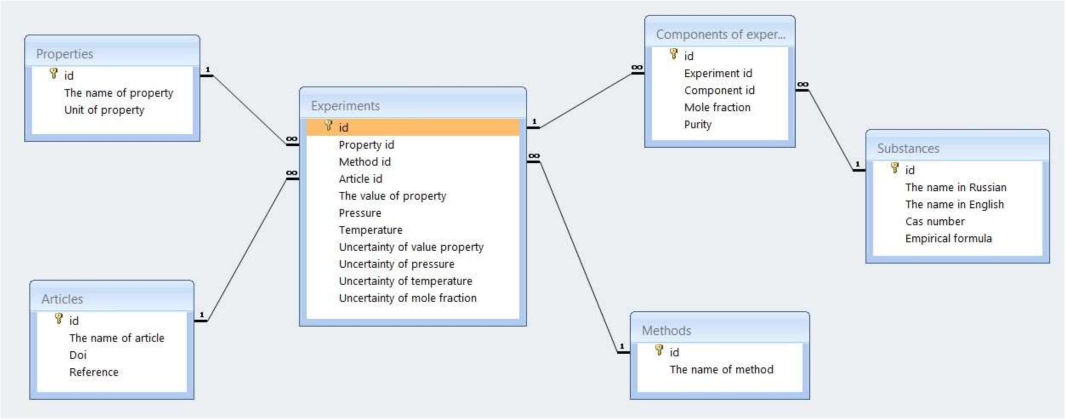

Figure 1. The structure of database

The following properties were included in database: density, isobaric heat capacity, viscosity, speed of sound, thermal conductivity, surface tension, refractive index. The database displays the dependence of the listed properties on temperature, concentration of solution components and pressure. The database pays special attention to the reliability of the values it contains. For each property, the experimental method is indicated, as well as the uncertainties of the properties and the conditions under which the measurements were made. Data search is carried out for two-component anhydrous DES or for their three-component systems with water. For this purpose, the program has created search lines with the ability to write down component systems in the form of common names in Russian or English, CAS numbers and empirical chemical formulas. It is possible to select systems with maximum or minimum property values under given conditions.The database also provides links to primary sources in the form of an article title and a link in doi format. The program has several reporting methods: in the form of tables and graphs. The structure of database is presented in Figure 1. The database was implemented in MySQL and was filled out through a form created using the Yii framework in PHP.

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DIFFUSION OF COMPONENTS IN COACERVATE PHASE OF AQUEOUS-SALT SYSTEMS CONTAINING POLYMERIZED IONIC LIQUID

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In recent decades, ionic liquids (ILs) with their unique properties are of special interest for synthesis of polymerized ionic liquids [1-3]. Polymerized ILs are the polyelectrolytes composed IL as a monomer unit. Due to the combination of properties of ILs and polyelectrolytes, polymerized ILs are used for the preparation of functional materials, the development of methods for analysis, synthesis and catalysis, the design of electrochemical devices, etc. [1-3]. A particular attention is paid to apply such polyelectrolytes in the composition of aqueous-salt biphasic systems for the extraction of biomolecules [4]. For their specific application, structural design is required [5]. Indeed, the rational design may help to find the polymerized ILs structures with different phase behavior in aqueous or aqueous-salt solutions. For water-soluble polymerized ILs, an addition of salting out salts results in formation of aqueous biphasic systems (ABSs) [6]. ABSs are considered as media for the highly effective extraction of various solutes including biomolecules. In general, the extraction efficiency is determined by the affinity of the polyelectrolyte-rich (i.e. coacervate) phase to the solute and, in particular, is up to the structural behavior of the phase.

In this work, we consider the structural behavior of aqueous and aqueous-salt solutions of the polymerized IL, poly(1-butyl-3-vinylimidazolium bromide), in the presence/absence of L-tryptophan and vanillin (as model biocomponents). Polymerized IL was synthesized and characterized by ^{1}H - NMR and by thermogravimetric analysis. Moreover, the viscosities and surface tension data were obtained for aqueous and aqueous-salt solutions of poly(1-butyl-3-vinylimidazolium bromide) in the dilute concentration range. Diffusion of the components have been studied experimentally by dynamic light scattering and PGSTE - NMR spectroscopy and simulated by Molecular Dynamics. By means of MD modeling, we obtain the data on conformation and local structure of polyelectrolyte chains, diffusion and binding of counterions (bromide, L-tryptophanate). We discuss the results for two concentration regimes, i.e. dilute and concentrated. Note that the compositions of the studied concentrated solutions are close to the composition of the polymer-rich phase of the ABS.

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The financial support of the reported study was provided by the Russian Science Foundation, project number 20-13-00038. NMR measurements were performed at the Center for Magnetic Resonance of the Research Park of St. Petersburg State University.

SOLVATION OF HYDROCARBONS IN TRIETHYLAMMONIUM BASED PROTIC IONIC LIQUIDS

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Ionic liquids are promising solvents for many separation and extraction processes. A large number of combinations of cations and anions allows to tune the properties of the solvent for specific tasks. Among the variety of ionic liquids, protic ionic liquids (PILs) can be distinguished, the synthesis of which is relatively simple and cheap. A large number of studies compare the solvation properties of aprotic ionic liquids and traditional solvents such as sulfolane and N-methylpyrrolidone. However, the solvation properties of various protic ionic liquids remain poorly explored.

In this work, the activity coefficients of hydrocarbons in protic ionic liquids based on triethylamine and acetic acid, trifluoroacetic acid, and triflic acid were measured. The gas chromatographic headspace analysis was used to experimentally determine the activity coefficients at 298 K.

Hydrocarbons have a significant solubility in triethylammonium acetate, trifluoroacetate, and triflate. Triethylammonium acetate and trifluoroacetate have modest selectivity for n-hexane/benzene separation, while triethylammonium triflate has higher selectivity and capacity for benzene than sulfolane, a solvent commonly used for the extraction of aromatic hydrocarbons from hydrocarbons mixture. Further synthesis and thermochemical studies of novel PILs and solutions in them can result in the discovery of innovative solutions for industrial separation problems.

The study was supported by the Russian Science Foundation project 24-13-00062.

THERMODYNAMICS OF THREE-COMPONENT LAVES PHASES FORMED BY IRON, CHROMIUM, SILICON, NIOBIUM AND MOLYBDENUM

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There is a large group of intermetallic compounds with the AB_2 structure called Laves phases (named after Fritz Laves). Laves phases tend to form extended solid solutions and can exist in several polytypes. The most common are hexagonal C14 ($MgZn_2$ structure type) and cubic C15 ($MgCu_2$ structure type). The ideal ratio of the atomic radii of components A and B is rA/rB= 1.225. Consequently, large Nb and Mo atoms tend to occupy positions A.

Optimization of the composition of the material aiming to avoid the formation of secondary phases at operating temperature is one of the most important problems solved during the development and production of iron-based steel. This issue becomes especially relevant in the case of brittle Laves phases due to their formation at high operating temperatures, which leads to a degradation of the mechanical properties of steels. In addition, increased interest in Laves phases is also associated with their ability to absorb up to four hydrogen atoms per formula unit, which makes them suitable for hydrogen storage.

The research is devoted to the experimental analysis of iron-based Laves phases in three ternary systems: Fe-Si-Nb, Fe-Si-Mo, Fe-Cr-Mo. Laves phases in ternary systems Fe-Cr-Nb and Fe-Nb-Mo were investigated by Jacob etal [1] and Zhou etal [2] respectively. Zhou etal [2] did not observe these phases in the Fe-Cr-Si system. The Fe-Si-Nb ternary system has been thermodynamically assessed in a number of works, but existing models assume significantly different regions of homogeneity of the Laves phase [4,5] than those determined experimentally. The only experimental work on the study of phase equilibria with the Laves phase in the Fe-Cr-Mo system was carried out in 1988 [3]. At the same time, there is no experimental data for the Fe-Si-Mo system.

In the present work, we attempt to determine the phase equilibria in mentioned above systems and the thermodynamic properties of Laves phases. All samples were obtained by arc melting. Microstructure studies were carried out in the cast and annealed states (900 °C, 1 week) using SEM and EPMA methods. Transformation temperatures were determined by differential thermal analysis (DTA). The enthalpies of formation of Laves phases were determined by drop solution calorimetry. The experimental data obtained during the work will be further used to build a modern national thermodynamic database.

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QUANTUM CHEMICAL MODELING MOLEKULES OF Bi_2O_3-B_2O_3-BaO AND Re:YAG COMPONENTS OF GLASS CERAMICS

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The study of the structure and spectral properties of $Bi_2O_3 – B_2O_3 –$ BaO glass, which is compatible in optical, thermophysical and physicochemical properties with the crystalline phase of yttrium aluminum garnet, is an urgent task for the creation of glass crystals for optical purposes. The experimentally established presence of a glass phase in ultra-dispersed samples of bismuth barium borate glasses $20Bi_2O_3 - x$BaO - $(80-x)B_2O_3$ $x = 5, 10, 20$ mol. % BaO with spherical particles makes it possible to use the so-called cluster approach, capable of reflecting the influence of edge effects on the IR spectrum during quantum chemical modeling of nano-sized particles.

To solve this problem, a quantum chemical study of the crystalline and glass components of luminescent glass ceramics, namely nano-sized yttrium aluminum garnet doped with rare earth ions, is proposed. A study of the glass component was carried out, namely, the geometry was optimized by the DFT method with the uB3LYP functional and the LanL2DZ basis set for the minimum potential energy for the glass structure of the composition $20Bi_2O_3 - x$BaO - $(80-x)B_2O_3$, containing x = 5, 10 and 20 mol. % BaO, and the geometry of the crystalline component was calculated: Er(Ce): $Y_3Al_5O_{12}$ by the DFT/uB3PW91/SDD method. For the obtained models, the IR spectra were calculated, and the absorption bands of the calculated wave numbers were compared with the measured ones.

The UV-vis spectrum was calculated for the $Y_5Ce_2Al_9O_{26}$ and $Y_5Er_2Al_9O_{26}$ fragments using the DFT/uB3PW91/SDD method. The energy gap values for YAG are 7.34 eV (169 nm), for the Ce:YAG molecule 6.87 eV (181 nm) and Er:YAG 2.1 eV (590 nm).

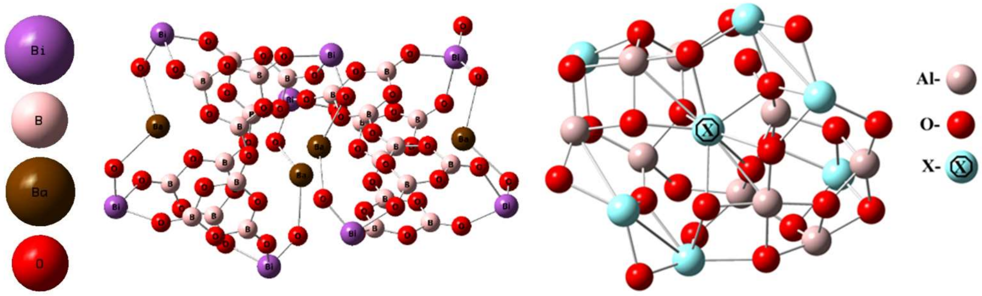

Figure 1. Calculated spatial structures of $20Bi_2O_3 - (80-x)B_2O_3 – x$BaO glasses and a fragment of the X-$Y_6Al_9O_{26}$ molecule, where X: Y, Ce, Er.

The results obtained confirm the possibility of constructing theoretical models based on quantum chemistry to describe the geometric structure, as well as the vibrational and electronic characterization of nano-sized glass-forming systems.

The study was supported by the Russian Science Foundation grant № 20-73-10110, https://rscf.ru/en/project/20-73-10110/.

SOLVATION OF *β*-ALANYL-*L*-HISTIDINE IN SOME WATER-ALCOHOLS MIXTURES AT T=298.15 K

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In continuation of thermochemical studies of the processes of dissolution and solvation of amino acids and peptides, in this work were obtained enthalpic characteristics of dissolution and solvation of β-alanyl-L-histidine (henceforth denoted as L-carnosine or β-Ala-L-His) in aqueous solutions of monatomic alcohols. L-carnosine is a dipeptide present in high concentrations in the tissues of living organisms, performing various protective functions. It is a powerful broad-spectrum antioxidant capable of protecting lipids, proteins and nucleic acids from oxidation. Monatomic alcohols (EtOH, 1-PrOH, 2-PrOH) were selected as solvents, which are denaturing agents of various strengths for globular proteins. Therefore, an important place in the disclosure of the mechanisms of denaturation of proteins and biopolymers is occupied by works studies devoted to the interaction between amino acids, simple peptides and alcohol molecules. The presented work had the following objectives: a) to study the influence of the structure of alcohols (EtOH, 1-PrOH, 2-PrOH) and their concentrations in aqueous solutions on the thermochemical characteristics of the dissolution and solvation of L-carnosine (in the range of 0 ÷ 0.25 mole fractions of alcohol and T = 298.15 K); b) to estimate the energy of intermolecular interactions of these peptides with EtOH, 1-PrOH and 2-PrOH molecules in aqueous solutions by calculating the enthalpic coefficients of pairwise interactions (h_{xy}); c) to quantify the contributions of the side chains of β-Ala-L-His and β-alanyl-β-alanine (henceforth denoted as β-Ala-β-Ala); d) to get new experimental data in the field of solutions amino acids and peptides. The tasks were solved by measuring (by calorimetry) and analyzing the enthalpy of dissolution of L-carnosine, which were used to calculate the standard values of the enthalpy of dissolution, transfer and solvation of these substances from water to water-alcohol mixtures, as well as the enthalpic coefficients of pairwise interactions (h_{xy}) with EtOH, 1-PrOH and 2-PrOH molecules. The obtained data are of interest in predicting optimal conditions for the existence of stable forms of protein components in water-organic media used in biocatalytic processes.

The principal conclusions concerning to the solvation of β-Ala-L-His and β-Ala-β-Ala in mixtures of H_2O+ (EtOH, 1-PrOH and 2-PrOH) from this investigation are:

a)The enthalpies of solvation of β-Ala-L-His and β-Ala-β-Ala in the study mixtures demonstrate a strong dependence on the structure of the alcohol, its concentration in solution and the structure of the side chain in the dipeptide molecule.

b)An increase in the length of the hydrocarbon chain in an alcohol molecule, as well as the presence of alkyl groups in its molecule (their number and mutual arrangement), significantly affects the nature of intermolecular interactions with peptide molecules.

c)The dependences = f(x_2) of β-Ala-L-His and β-Ala-β-Ala in the same mixed solvents are similar, but β-Ala-L-His is solvated more strongly. This is probably due to the presence in its side chain of two hydrophilic centers capable of forming H-bonds with the molecules of the cosolvent.

d)The enthalpic coefficients of the pairwise interactions of β-Ala, β-Ala-β-Ala and β-Ala-L-His are equally dependent on the hydrophobic properties of alcohols. Their endothermicity increases in series: EtOH < 1-PrOH < 2-PrOH.

CHOOSING APPROPRIATE FORCE FIELD FOR MOLECULAR DYNAMICS SIMULATIONS OF LIQUID MEMBRANES

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We compare GAFF, OPLS-AA/CM1A, CHARMM36, and COMPASS force fields to determine the most appropriate force field for simulating ether-based liquid ion-selective membranes. Using the selected force fields, we calculate density and shear viscosity of diisopropyl ether (DIPE) across a temperature range of 243–333 K. Calculation results are shown in Figure 1.

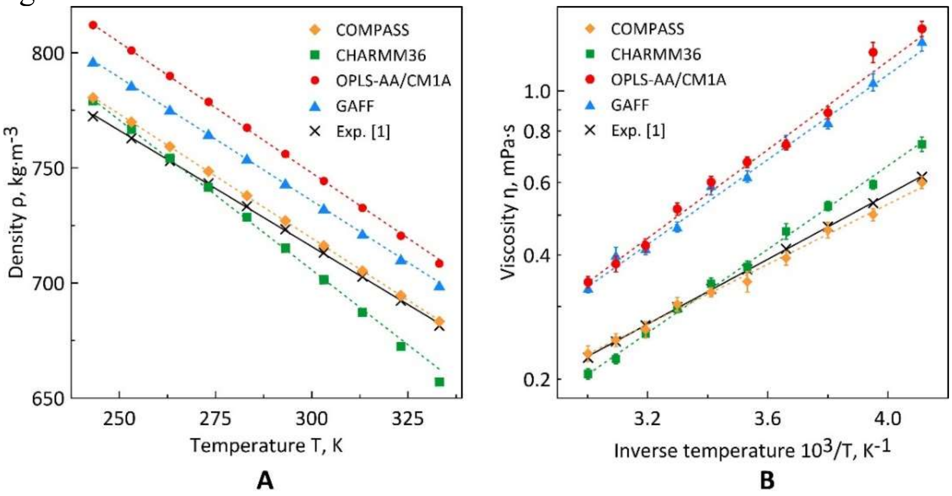

Figure 1. Temperature dependencies DIPE density (A) and shear viscosity (B)

GAFF and OPLS-AA showed similar results. They overestimate density by 3-5 % and shear viscosity by 60-130 %. CHARMM36 yields error of 1-4 % for density and 10-20 % at 243-273 K and 2-9 % at 283-333 K for shear viscosity. COMPASS yields errors less than 1 % for density and 1-6 % for shear viscosity. Preliminary results on density and viscosity were published in [2].

We also use the CHARMM36 and COMPASS force fields to evaluate the mutual solubility of water and DIPE, as well as the partition coefficients of ethanol in water–DIPE solution. CHARMM36 underestimates DIPE solubility in water by an order of magnitude and falls into the same order of magnitude for water solubility in DIPE and ethanol partition coefficients. COMPASS underestimates DIPE solubility in water by two orders of magnitude, water solubility in DIPE by one order of magnitude, and yields an error of one order of magnitude for ethanol partition coefficients. Based on our comparison results, we conclude that CHARMM36 is the most suitable force field for modeling ether-based liquid membranes.

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THE FORMATION OF COMPLEXES OF GLUTATHIONE WITH NUCLEIC BASES OF THE PYRIMIDINE SERIES IN A BUFFERED SALINE

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Glutathione (reduced) is a tripeptide composed of the following sequence: γ-L-glutamyl-L-cysteinyl-glycine. This peptide is involved in numerous metabolic processes, such as protein biosynthesis on RNA, protein restoration during oxidative stress, and conjugation with lipophilic xenobiotics.

In aqueous solution, glutathione takes on various ionic forms. We calculated the distribution of ionic forms depending on pH based on known data on acid dissociation constants. In an aqueous solution at pH = 7.4, the dominant forms of the peptide are a tripolar anion (mole fraction is 0.95) and a doubly charged anion (mole fraction is 0.05). The tripolar anionic form contains 2 negatively charged carboxylate groups and 1 positively charged amino group.

In this work the investigation the complex formation of glutathione with pyrimidine nucleic bases (uracil, thymine, and cytosine) in a phosphate buffered saline (pH=7.4) have been performed by calorimetric method. Data on initial reactant concentrations and experimental values of the transfer enthalpy were used to simultaneously calculate apparent constants of complexation and enthalpy change ($\log K_r$ and $\Delta_r H$), as enabled by the HEAT computer program [1]. As a result, we obtained a complete set of thermodynamic parameters of complexation, including the Gibbs energy, enthalpy and entropy of the process.

Complexes of uracil exhibit a greater stability compared to cytosine complexes. Strengthening the hydrophobic properties of the nucleic base from uracil to thymine due to the additional CH_3 group also causes an increase in the favorable entropy factor in the complexation with peptides and in the stability of complexes.

Hydrogen bonding and hydrophobic interaction play a significant role in the formation of glutathione complexes with pyrimidine bases. The formation of hydrogen bonds between peptides and pyrimidine bases was proven by quantum chemical modeling [2]. The hydrophobic effect during complexation is confirmed by the entropy characteristics and temperature derivatives of the standard molar volume of the nucleic base upon addition of peptides [3].

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COMPLEXES OF IONIZED ALANYL-L-TYROSINE AND GLUTATHIONE WITH PYRIMIDINE NUCLEOBASES. DFT-CALCULATIONS AND TOPOLOGY ANALYSIS

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The intricate interaction between proteins and DNA lies at the heart of numerous biological processes, dictating gene expression, regulation, and cellular functions. Understanding the nuances of protein-DNA complexes not only advances our comprehension of fundamental cellular processes but also holds profound implications for therapeutic interventions and biotechnological applications.

Density Functional Theory (DFT) calculations have been employed to investigate the complex formation of nucleic bases (cytosine, uracyl and thymine) with peptides - alanyl-L-tyrosine (Ala-Tyr) zwitter-ion and glutathione (GSH) tripolar anion. The computer simulation of the studied objects is performed by the B97D/6-311++G(3d,3p) method implemented in the Gaussian09 package. The structure optimization and the energy calculation of initial molecules and complexes were carried out with regard to effects of the electrostatic interaction with polarizable medium (with water properties) within the PCM model. To investigate hydrogen and non-covalent interactions in the complexes, the QTAIM analysis implemented in the Multiwfn 3.3.8 program was carried out.

Four configurations of (AlaTyr + Cyt) complexe and two configurations of (AlaTyr + Ur) complexe are distinguished. The optimized structures of the complexes corresponding to the energy and free Gibbs energy minima are stabilized by hydrogen bonds. In the complexes, peptides act as polydentate ligands. In the peptide, sites of the hydrogen bonding are charged NH_3^+ and COO^- groups at the ends of the peptide main as well as polar fragment of the amide fragment in the middle of the chain. The lengths of hydrogen bonds are within 1.573-1.735 A; hydrogen bond energies vary from -3.3 kcal/mol to -12.6 kcal/mol. In the complex, the sum of hydrogen bond energies calculated by BCPs is comparable with the contribution of intermolecular interaction energies calculated as the difference of the complex energy and the energies of its components with the same structure. The more energetically favorable structures of complexes were selected in accordance of minimum of the Gibbs energy of complexation. The effects of hydrogen bonding and stacking interactions between the aromatic rings of the nucleobase and the side group of the peptide compete with each other in AlaTyr + Cyt complexes. The orientations of the peptide and nucleic base that are favorable for these two types of interactions do not coincide. In the structure of complex IV (AlaTyr + Cyt), both the hydrogen bond and the stacking effect partially occur simultaneously, but in complex II (AlaTyr + Cyt) II, which has the most negative values of ΔE_{comp} and ΔG_{comp}, the hydrogen bonds predominate.

The anionic form of glutathione tripeptide is capable of forming a greater number of H-bonds with pyrimidine bases; In the complexes, from 2 to 4 intermolecular H-bonds are recorded. The following peptide sites exhibit H-bonding ability: one NH_3^+, two COO^- groups, and two amide fragment in the middle of the chain. The H-binding sites in nucleic bases are the NH_2 group (in cytosine), the carbonyl O atom, and the HH fragment. The structures of glutathione complexes with uracil and its methyl derivative, thymine, are similar. But the Gibbs free energy of the complexation process is more favorable in the case of thymine due to the increase in the negative contribution of the energy of intermolecular interaction.

THE INVESTIGATION OF THE FORMATION ENTHALPY OF RARE-EARTH HAFNATES

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The study of oxides containing rare earth metals and Hf is an urgent and complex task. These materials have found a large number of applications: from processing nuclear waste to creating thermal barrier coatings. Compounds with pyrochlore and fluorite structures from the RE_2O_3-HfO_2 system are of the greatest interest. However, the phase relationships of the corresponding systems are difficult to study experimentally due to the extremely high temperatures of phase transformations and the long time required to reach equilibrium. In this case, the experimental study of thermodynamic properties and the application of CALPHAD methods can be extremely useful for establishing the nature of phase equilibria in the corresponding systems. The purpose of this work was to obtain enthalpies of formation of hafnates with rare earth elements using drop-solution calorimetry methods. Compounds having both pyrochlore and fluorite structures were prepared using the inverse coprecipitation method and characterized by SEM/EDX and XRD. Dependences of the enthalpies of formation of compounds with the structure of pyrochlore and fluorite from the ionic radius of the rare earth element were analyzed. The enthalpy of formation becomes more positive with decreasing ionic radius, which is consistent with results previously observed for titanates and zirconates.

The study was supported by Russian Science Foundation project № 18-13-00025.

DATA EXCHANGE FILE FORMAT FOR GATHERING THERMOPHYSICAL AND THERMOCHEMICAL EXPERIMENTAL OF MATERIALS

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Efforts to develop a standard for the exchange of data on thermophysical and thermochemical properties began in the early 1980s by adapting the use of electronic databases. Several approaches have been developed (such as COSTAT, ELDATA, ThermoML), each of which has its own limitations for implementation, due to the corresponding level of development of computer systems and user interfaces.

In recent years, the choice of data exchange format has been made based on various criteria, such as human readability, the availability of widely used editing software, and the ability to construct a diagram. Human-readable formats make it easier for editors and reviewers to review submitted data and check for consistency and possible errors. The availability of widely used editing software reduces the need to learn new ways to edit submitted files and reduces the need for a new kind of software needed to implement the format into a database workflow. The schema allows for the use of tools such as automated validators and reduces the need for human interception in the process of adapting submitted data into electronic databases.

This work presents a new approach to standardize a data exchange format based on multiple CSV files. The format is mainly adapted for collecting thermochemical and thermophysical data, such as: phase diagram data, data on crystal structure and various calorimetric properties of substances. File organization rules and naming conventions are discussed. The presented format is designed to be extensible, and various ways to extend the presented format for mechanical and other table properties are discussed. Recommendations for adapting the formatted files for the journal submission process and possible use cases for web applications built from the collected data files are presented.

The research was funded by the grant Russian Science Foundation № 23-13-00138.

THERMODYNAMIC PROPERTIES OF $Na_3Cr_2(AsO_4)_3$ WITH GARNET-LIKE STRUCTURE

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One of the promising materials for the ceramic industry is mineral like compounds with garnet structure. Compounds with garnet structure have general formula of $A_3B_2(XO_4)_3$, where A are cations in oxidation states from +1 to +4 and ionic radii 0.9−1.1 Å, B are cations with ionic radii 0.5−0.8 Å and oxidation states from +2 to +4, X elements with ionic radii 0.3−0.5 Å. There are a lot of synthetic and natural compounds and their synthesis methods described in literature, but it is very little information about thermodynamic properties, which can help to better understanding of correlation between structure and thermal properties.

This is why the goal of this work is to determine the temperature dependence of heat capacity $C^{\circ}_{p,m} = f(T)$ of polycrystalline $Na_3Cr_2(AsO_4)_3$ using precise adiabatic calorimetry method in the range of T = (5 and 323) K, calculate standard thermodynamic functions $C^{\circ}_{p,m}$, $\Delta_0^T H^0_m$, $\Delta_0^T S^0_m$ and $\Delta_0^T G^0_m$ in temperature range from 0 to 323 K.

$Na_3Cr_2(AsO_4)_3$ was prepared via the co-precipitation method. Experimental diffraction data of the sample confirms that prepared compound is single-phase $Na_3Cr_2(AsO_4)_3$ (purity more than 99%) with the garnet structure (pr. gr. *Ia*3*d*). The heat capacity of $Na_3Cr_2(AsO_4)_3$ (Figure) rises with increasing temperature, except for the exothermic effect around 20 K.

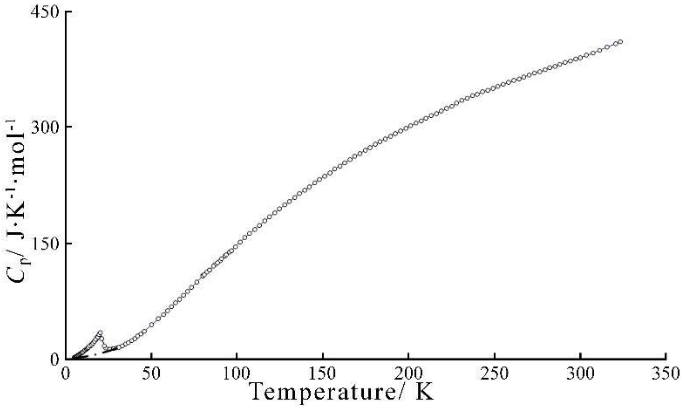

Figure. Temperature dependence of heat capacity of $Na_3Cr_2(AsO_4)_3$.

The exothermic effect starts at 5 K and ends at 27 K with $\Delta_{trs}H_m$ = 218.3 J/mol. The heat capacity anomaly can be associated with the antiferromagnetic ordering process [1]. This transition could be very useful to the microelectronics industry as a form of memory storage.

The standard thermodynamic functions of $Na_3Cr_2(AsO_4)_3$ were calculated from the $C^o_{p,m}(T)$ values over the range from T→0 K to 323 K . $C^o_{p,m}$ values were extrapolated stating from T = 6 K to T → 0 K according to Debye's law. The standard molar specific thermodynamic functions at 298.15 K and 0.1 MPa were determined to be $\Delta_0^T H^0_m = 63.08\, kJ \cdot mol^{-1}, \Delta_0^T S^0_m = 392.3\, J \cdot K^{-1} \cdot mol^{-1}\ and\ \Delta_0^T G^0_m = 53.87\, kJ \cdot mol^{-1}$.

[1] L. Abello, K. Chhor and M. Bar, *Journal of materials science*, 1989, 24, 3380-3386.

This work was was supported by Russian Science Foundation grant № 23-23-00044, https://rscf.ru/project/23-23-00044/.

THERMAL EXPANSION AND PHASE TRANSITION OF GARNET STRUCTURED LITHIUM-CHROMIUM ARSENATE-PHOSPHATE

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Mineral-like garnet structured compounds are one of the promising candidates for microelectronics, in LED's production and in the field of radioactive waste management. Garnet structure defines with a general formula $^{VIII}A_3{}^{VI}B_2{}^{IV}X_3O_{12}$, where A are cations with ion radii from 0.9 **Å** to 1.1 **Å** and in oxidation states from +1 to +4, B are smaller cations with oxidation states +2, +3, +4, X are elements which are capable of forming tetrahedral anions (Al, Fe, Ga, Si, Ge, Sn, V, As), while VIII, VI and IV are co-ordination numbers in these positions. Wide range of cationic substitution of garnets gives an opportunity for deep investigation of thermal properties in range of chemical composition in form of solid solution.

The purpose of this work is the synthesis of arsenate-phosphates in the system $Li_3Cr_2(AsO_4)_x(PO_4)_{3-x}$ ($2.0 \le x \le 3$) and examination of their thermal behavior.

Single phase samples of composition $Li_3Cr_2(AsO_4)_x(PO_4)_{3-x}$ ($2.0 \le x \le 3.0$) have been obtained by co-deposition of salts containing the elements forming the target product. Experimental diffraction data of the samples confirms that they are single phases with the garnet structure. The chemical composition and homogeneity of the samples were confirmed by using a high-resolution scanning electron microscope and microprobe analysis.

Samples (purity more than 99%) were studied by the synchronous TG−DSC analysis. The DSC curves showed endothermic effects. The first effect is due to the transformation of a low-temperature modification with the garnet structure (I) into a high-temperature form of a rhombohedral structure (II). Subsequent effects are responsible for thermal decomposition. Temperatures of first and second effects are 1173, 1204, 1239 K and 1276, 1289, 1317 K for samples with $x = 2.0, 2.5, 3.0$ correspondingly.

The parameters of thermal expansion of arsenate-phosphates were determined by the method of thermorentgenography in the range from 143 K to 473 K. Arsenate-phosphates expand isotropically with changes in temperature because all samples have a cubic structure. Their linear coefficient of thermal expansion is positive (table 1).

Table 1. Linear thermal expansion coefficients in the region of 173–473 K

Compound	$\alpha \cdot 10^6/K^{-1}$
$Li_3Cr_2(AsO_4)_2(PO_4)$	7.5
$Li_3Cr_2(AsO_4)_{2.5}(PO_4)_{0.5}$	8.4
$Li_3Cr_2(AsO_4)_3$	16.7

Based on the calculated linear thermal expansion coefficients, the resulting samples can be classified as moderate expansion type.

This work was This work was supported by Russian Science Foundation grant № 23-23-00044, https://rscf.ru/project/23-23-00044/.

ENTHALPIES OF FORMATION OF $RCoO_{3-\delta}$ PEROVSKITE COBALTITES

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Standard enthalpies of formation at 298.15 K, $\Delta_{f,\,298\ K}H°$, for $RCoO_{3-\delta}$ (R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y) perovskite-type rare-earth cobaltites were obtained from the combined results of drop calorimetry and reduction in a TG-DSC setup. The relationship between the oxygen nonstoichiometry, δ, and thermodynamics of $RCoO_{3-\delta}$ was discussed. The trend towards decreasing stability with decreasing ionic radius of R^{3+} due to increasing enthalpy of formation from binary oxides (CoO and R_2O_3), $\Delta_{f,\,ox,\,298\ K}H°$, was confirmed for the whole $RCoO_{3-\delta}$ series. Drop calorimetry results were also used in discussing, comparing and assessing the literature heat capacity, $C_p(T)$, data for $RCoO_{3-\delta}$ ($R \neq Y$). For $YCoO_{3-\delta}$, both $\Delta_{f,\,298\ K}H°$ and $C_p(T)$ were obtained for the first time solely from the drop calorimetric results; $\Delta_{f,\,298\ K}H°$ values determined by two different methods perfectly agree with each other. The reference data and $C_p(T)$ of $RCoO_{3-\delta}$ were used to calculate $\Delta_{f,\,298\ K}H°$ from the published EMF measurement results. Finally, the available $\Delta_{f,\,ox,\,298\ K}H°(RCoO_{3-\delta})$ values were compared, and the unusual dependence of $\Delta_{f,\,298\ K}H°(LaCoO_{3-\delta})$ on the heat treatment history was identified and supported by the additional isoperibolic solution calorimetry measurements.

This work was financially supported by the Russian Science Foundation (grant № 24-23-00478).

DEFECT CHEMISTRY AND THERMODYNAMICS OF MIXED CONDUCTING PEROVSKITE-TYPE OXIDES $SrTi_{1-x}Fe_xO_{3-\delta}$

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Mixed ionic- and electronic-conducting perovskite-type oxides are the state-of-the-art materials for high-temperature solid-state electrochemical devices such as solid oxide fuel cells (SOFCs), oxygen membranes and sensors. The oxides $SrTi_{1-x}Fe_xO_{3-\delta}$ have received a lot of attention as promising materials for such applications. They are capable of oxygen exchange with surrounding atmosphere. This results in strong dependence of their oxygen content on temperature (T) and oxygen partial pressure (pO_2) as well as in strong variation of other properties including the thermodynamic ones. As a result, the detailed understanding of the defect chemistry of these materials is of high importance for understanding their properties. However, these data for $SrTi_{1-x}Fe_xO_{3-\delta}$ oxides are very restricted to date. Therefore, the main aim of this work was to perform detailed study of the relationship between the thermodynamics of defects in $SrTi_{1-x}Fe_xO_{3-\delta}$ oxides and their various properties such as oxygen nonstoichiometry, oxidation enthalpy, heat capacity, total conductivity, Seebeck coefficient etc.

Powder samples of $SrTi_{1-x}Fe_xO_{3-\delta}$ ($x = 0.3–0.7$) were synthesized using the standard ceramic and spray-pyrolysis techniques. Phase-purity of the samples was confirmed by X-ray diffraction (XRD) with 7000S diffractometer (Shimadzu, Japan) in Cu Kα radiation.

Oxygen nonstoichiometry, total conductivity, Seebeck coefficient, oxidation enthalpy, enthalpy increments and thermal and chemical expansion of perovskite-type oxides $SrTi_{1-x}Fe_xO_{3-\delta}$ ($x = 0.3–0.7$) were studied as functions of oxygen partial pressure $-5 < \log(pO_2/\text{atm}) < 0$ and temperature $600 < T/°C < 1050$. The extensive defect chemical modelling was carried out. As a result, the dominating defect species were identified, and thermodynamic functions of the corresponding defect reactions were determined. This allowed obtaining the self-consistent set of parameters describing the variation of various measured properties of $SrTi_{1-x}Fe_xO_{3-\delta}$ oxides with T and pO_2.

This work was supported by the Russian Science foundation (grant No. 24-23-00487).

CHEMICAL AND PHASE TRANSFORMATIONS DURING THE SYNTHESIS OF GLASS-CERAMICS BASED ON Bi_2O_3-BaO-B_2O_3 AND ER:YAG

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Particularly popular among optical materials are ceramics based on yttrium aluminum garnet doped with rare earth ions (RE:YAG). The main problem in this direction is to obtain materials with zero porosity and high phase and chemical purity. A possible decision is the development of glass-ceramic materials based on Er:YAG, where the glass component is borate glass of the Bi_2O_3–BaO–B_2O_3 system, close to YAG in density and refractive index.

The purpose of the work was to obtain and study the features of the formation of glass-ceramics based on Bi_2O_3-BaO-B_2O_3 and Er:YAG from an ultradisperse charge.

The synthesis of the charge was carried out in an original laboratory installation for ultrasonic sputtering of a multicomponent solution in three stages: 1) production of glass-forming material of the composition $20Bi_2O_3$-20BaO-$60B_2O_3$, close in density and refractive index to erbium-substituted garnet; 2) obtaining the crystalline component of $(Er_{0.5}Y_{0.5})$AG in the form of a binary hydrosol; 3) formation of the charge by mixing the glass phase from step 1) and the hydrosol from step 2) in a molar ratio of $46(20Bi_2O_3$-20BaO-$60B_2O_3)$–$54(Er_{0.5}Y_{0.5})$AG.

Phase and chemical transformations of the formed materials were discovered and studied (Figure 1) by synchronous thermal analysis (STA) and X-ray phase analysis (XRD). According to the results obtained, the recommended mode of ultradisperse mixture heat treatment for producing glass-ceramics using the developed method does not exceed a temperature of 1375 K.

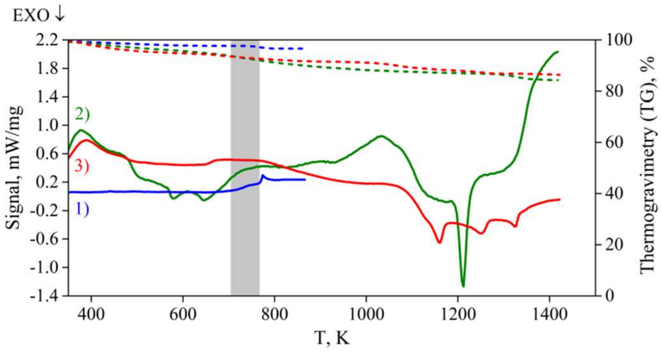

Figure 1. The synthesis of the charge was carried out in an original laboratory installation for ultrasonic sputtering of a multicomponent solution in three stages: 1) production of glass-forming material of the composition $20Bi_2O_3$-20BaO-$60B_2O_3$, close in density and refractive index to erbium-substituted garnet; 2) obtaining the crystalline component of $(Er_{0.5}Y_{0.5})$AG in the form of a binary hydrosol; 3) formation of the charge by mixing the glass phase from step 1) and the hydrosol from step 2) in a molar ratio of $46(20Bi_2O_3$-20BaO-$60B_2O_3)$–$54(Er_{0.5}Y_{0.5})$AG.

The conditions for the formation of crystalline phases of garnet and yttrium borate from an ultradisperse charge were determined by the method of minimizing the Gibbs energy.

This work was supported by the Russian Science Foundation (grant No. 20-73-10110).

THERMODYNAMIC MODELING OF SYSTEMS WITH LIQUID CRYSTALS (ON THE EXAMPLE OF CHOLESTEROL DERIVATIVES)

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Cholesteric liquid crystals (LC) are widely used in thermography, chemical sensors and bistable displays. LC - solvent systems are important both for the purification of mesogens and in the selection of additives in LC materials.

Mesomorphic cholesteryl esters with the general formula Ch-OOC-R (R = C_nH_{2n+1}, Ch-Cn, n = 4-6, 8, 10) were selected as objects of study. Using thermal analysis methods systems with 1,4-xylene were studied, T-x diagrams of the systems were obtained and the coordinates of invariant points were determined.

LC solubility curves in solvents of different polarity were studied. Based on the obtained dependences of the mole fraction of LC in a saturated solution X_1 on temperature T the enthalpies of dissolution Δ_sH were calculated:

$\ln X_1 = a - b/T$ ($b = \Delta_sH/R$).

Figure 1 shows the solubility polytherms of Ch-C4 in the temperature range from 0 to 45 °C in solvents of different polarities (n-hexane (1), n-heptane (2), cyclohexane (3), methylcyclohexane (4), benzene (5), toluene (6), ethyl acetate (10)).

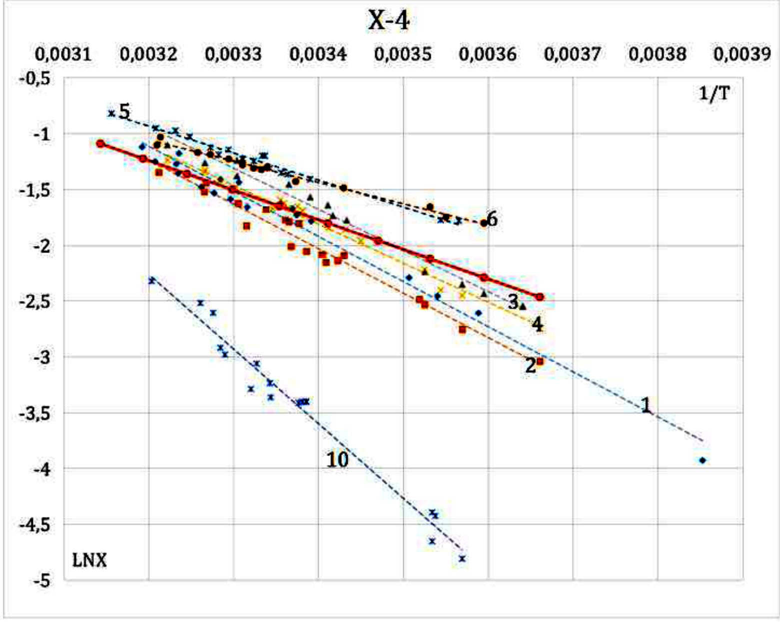

Figure 1. Solubility polytherms of Ch-C4.

Using group-contribution schemes the Hildebrand solubility parameters (δ_i) and Hansen solubility parameters (δ_{di}, δ_{pi}, δ_{hi}) of mesogens were calculated. Depending on the choice of calculation scheme the values of δ LC lie in the range of 16.3 ÷ 17.1 $MPa^{0.5}$, which explains the abnormally high solubility in alkanes compared to other classes of LC. We also note the low solubility of LC in ethyl acetate (a traditional solvent for the crystallization purification of mesogens). Teas triangles were constructed to estimate LC solubility at 298 K. Hansen solubility parameters for solvents were taken from [1].

[1] Hansen C.M., *Hansen solubility parameters: a user's handbook,* 2007, 519 p. Boca Raton: CRC Press.

QSPR-METHOD OF PREDICTION OF VAPORIZATION ENTHALPIES OF ALKYLBENZENES

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Alkylbenzenes occupy an important place in the chemical industry. Oil additives, plasticizers, polymers, etc. are produced on their basis. At the same time, at the stages of production and separation of alkylbenzenes, it is necessary to have information about a number of their thermodynamic properties, including the enthalpy of vaporization. Since the number of alkylaromatic compounds is huge, it is difficult to obtain experimental data for them, and forecasting methods come to the rescue.

This paper presents the QSPR method for predicting the values of the enthalpy of evaporation of alkylbenzenes, based on the author's method [1-2].

A method is based on graph theory and available literature data on $\Delta_{vap}H_m{}^o(298.2)$ and $\Delta_l^g Cp^o(298.2)$. The calculation procedure is based on the linear dependence $\Delta_{vap}H_m{}^o(298.2)$ and $\Delta_l^g Cp^o(298.2)$ of total index ${}^{0-3}\chi$ determined by equation:

The index ${}^{0-3}\chi$ is the contribution from the molecular structure estimated by connectivity indices from zero to the third order ${}^{0-3}\chi_f = {}^0\chi + \frac{{}^1\chi}{2} + \frac{{}^2\chi}{3} + \frac{{}^3\chi}{4}$, ${}^0\chi = \sum_1^n 1/Ln(\delta_i)$ - is the zero order connectivity index and determines the contribution of atoms or a group of atoms; ${}^1\chi = \sum_1^m 1/Ln(\delta_i\delta_j)$ - is the first order connectivity index and determines the contribution of two valently bonded atoms; ${}^2\chi = \sum_1^p 1/Ln(\delta_i\delta_j\delta_k)$ - is the second order connectivity index and determines the contribution to the three successively located atoms; ${}^3\chi = \sum_1^r 1/Ln(\delta_i\delta_j\delta_k\delta_l)$ - is the third order connectivity index and determines the contribution to the four successively located atoms. Values of descriptors present in table 1.

Table 1. The values of descriptors.

Descriptor	Value	Descriptor	Value
$—CH_3$	1,4773	—C—	7,5949
$—CH_2—$	1,6201	-Car-	1,6914
—CH—	2,3685		

A vaporization enthalpy $\Delta_{vap}H_m{}^o(298.2)$ and difference of the molar heat capacities of the gaseous and the liquid phase $\Delta_l^g Cp^o(298.2)$ were estimated by equations:

$$\Delta_{vap}H_m{}^o(298.2) = 1{,}6883 \cdot {}^{0-3}\chi + 2{,}0781 \qquad \Delta_l^g Cp^o(298.2) = -2.416 \cdot {}^{0-3}\chi - 11.0$$

[1] E.L. Krasnykh and S.V. Portnova, *Journal of Structural Chemistry*, 2017, 58, 6, 706.
[2] E.L. Krasnykh and S.V. Portnova, *Journal of Structural Chemistry*, 2016, 57, 3, 437.

ENTHALPIES OF FORMATION OF SOME IONIC LIQUIDS

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Ionic liquids (ILs) are a class of compounds whose properties are currently being actively studied. High melting points and low volatility lead to the fact that most ILs either do not ignite or do not burn completely under normal conditions of a thermochemical experiment. As a result, despite a large number of studies in which the properties of ILs have been investigated, their enthalpies of combustion and enthalpies of formation are less known.

S.P. Verevkin et al. [1, 2] were for the first time able to measure the heat of combustion of two ionic liquids of 1-ethyl-3-methylimidazolium dicyanamide ($[C_2MIM][N(CN)_2]$) and 1-butyl-3-methylimidazolium ($[C_4MIM][N(CN)_2]$) in polyethylene ampoules and calculate their enthalpies of combustion and enthalpies of formation. The enthalpies of combustion of these liquids turned out to be –4955.4 ± 3.0 and –6285.1 ± 2.1 kJ/mol, and the enthalpies of formation were 235.3 ± 3.1 and 206.2 ± 2.5 kJ/mol, respectively [1, 2].

In this work, using IKA C 6000 isoperibol calorimeters, the enthalpies of combustion of three ILs: trihexyltetradecylphosphonium bromide ($[P_{66614}]Br$), butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{4111}][NTf_2]$) and 1-butyl-4-methylpyridinium tetrafluoroborate ($[BMPy][BF_4]$) were measured. Based on these values, their enthalpies of formation were calculated using thermochemical equations for the combustion of ILs.

For $[P_{66614}]Br$, the combustion reaction equation, for example, has the form:

$$C_{32}H_{68}BrP_{(l)} + 50\,O_{2(g)} = 32\,CO_{2(g)} + 32\,H_2O_{(l)} + HBr_{(s,H_2O)} + H_3PO_{4(s,H_2O)}. \quad (1)$$

Based on equation (1), the enthalpy of formation $\Delta_f H^o$ of $[P_{66614}]Br$ is equal to:

$$\Delta_f H^o(C_{32}H_{68}BrP_{(l)}) = 32\,\Delta_f H^o(CO_{2(g)}) + 32\Delta H^o(H_2O_{(l)}) + \Delta_f H^o(HBr_{(s,\,H_2O)}) + \Delta_f H^o(H_3PO_{4(s,H_2O)}) - \Delta_c H^o(C_{32}H_{68}BrP_{(l)}) \quad (2)$$

The reference values of the enthalpies of formation of substances necessary for calculating the enthalpies of formation of ILs according to equation (2) were taken from the literature [3,4].

For each IL, 10 experiments were carried out on the combustion of samples in the range from ~0.1 to ~0.5 g. As a result of the calculations for three ILs: $[P_{66614}]Br$, $[N_{4111}][NTf_2]$ and $[BMPy][BF_4]$, respectively, we obtained the following enthalpies of formation: –1197 ± 76, –1540 ± 33 and –1716 ± 17 kJ/mol.

The negative enthalpies of formation of $[P_{66614}]Br$, $[N_{4111}][NTf_2]$ and $[BMPy][BF_4]$ differ from the above positive enthalpies of formation $[C_2MIM][N(CN)_2]$) and $[C_4MIM][N(CN)_2]$), obtained in the works of S.P. Verevkin *et al.* [1,2].

[1] S.P. Verevkin, V.N. Emel'yanenko, D.H. Zaitsau, A. Heintz, C.D. Muzny, M. Frenkelb, *Phys. Chem. Chem. Phys.*, 2010, 12, 14994.
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[3] Electronic reference book: database of possible thermal constants of substances. URL: https://www.chem.msu.su/cgi-bin/tkv.pl?show=welcome.html (access date 03/01/24).
[4] Thermodynamic characteristics of substances (enthalpy, entropy, Gibbs energy, heat capacity) (reference table). URL: https://chemhelp.ru/handbook/tables/thermodynamic_data/ (access date 03/01/24).

HYBRID LIPOSOMES BASED ON PHOSPHATIDYLCHOLINE AND PYRROLIDINIUM SURFACTANTS: PHYSICOCHEMICAL AND BIOLOGICAL ASSESSMENTS

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Today the creation of drug delivery systems is a rapidly developing area of research. Liposomes have become well-known as drug carriers due to their low toxicity, high bioavailability, biodegradability, etc. The first liposomal drug was introduced on the market in 1995, and since then, many different types of vesicular systems have been developed. Surfactants are actively used as modifiers of liposomal systems, in particular, cationic surfactants, which are used to obtain positively charged liposomes that have an affinity for negatively charged biological targets (cells, tissues).

The aim of the study is to create hybrid liposomal nanocarriers based on phosphatidylcholine (PC) and cationic surfactants. The systems are designed for intranasal delivery of the acetylcholinesterase reactivator pralidoxime chloride (2-PAM) to the brain as part of the oxime therapy for organophosphate poisoning. New homologous series of cationic surfactants with a pyrrolidinium head group containing a hydroxyethyl fragment (MPS-n (OH), where n= 10, 12, 14, 16) were used for the liposome modification. At the first stage, the composition of hybrid liposomes was optimized under varying the hydrocarbon tail length of MPS-n(OH), the lipid/surfactant molar ratio, and the concentration of the loaded substances. It was shown that empty hybrid compositions had high stability (>2 months). Dynamic and electrophoretic light scattering (DLS) shown that the hydrodynamic diameter of the aggregates was in the range of 70-90 nm, the polydispersity index did not exceed 0.15, and the zeta potential values ranged from +10 to +55 mV. The change in the size and charge characteristics of traditional liposomes indicated the successful process of surfactant integration into the liposome bilayer and the formation of hybrid system. Transmission electron microscopy confirms the spherical shape of the aggregates, and the liposome size data are in good agreement with DLS data. Encapsulation of 2-PAM and the fluorescent probe rhodamine B (RdB) into the hybrid liposomes provided prolonged release of substrates *in vitro* compared with their free form. Encapsulation efficiency reached 85% and 67% for RdB and 2-PAM, respectively. The systems had low hemolytic activity and practically no tendency to hemagglutination. Thus, the physicochemical characteristics and *in vitro* biological activity of hybrid liposomes have been evaluated, and samples can be transferred for further *in vivo* tests on rats.

This work was financially supported by Russian Science Foundation (project № 23-73-10033).

RETENTION INDICES AND ENTHALPY OF SORPTION OF ESTERS OF 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL ALCOHOL AND DIBASIC CARBOXYLIC ACIDS

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Rubbers and plastics are known as unique materials due to their irreplaceable applications in machinery, medicine, construction, automotive industry, etc., and its applications are still in expansion. The aging of polymer materials is one the most important problems: due to aging, the deterioration of the outlook, hardness, physical and mechanical performances occures. To prolong the lifetime of polymer and rubber products by retarding their aging processes, antioxidants, based on hindered phenols, are used. [1]

One of the important variables in gas chromatography is the retention indices, based on retention time which is based on a function of experimental conditions. Retention indices suggested by Kovats are widely used in gas chromatography as data for further use in identification process and temperature programming conditions. Retention indices combine both: the relative retention and the specific retention volume. [2] The lack of data on Kovacs retention indices for the determination of hindered phenolic antioxidants makes their experimental determination with subsequent database adjustments relevant.

Experimental data was obtained for 10 partially and fully substituted esters of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol and dibasic carboxylic acids (oxalic, malonic, succinic, glutaric and adipic acids). All esters were obtained by esterification of alcohol and acids in self-catalysis mode. Chromatographic analysis was carried out on a Kristall-2000M gas-liquid chromatograph with Analyst 2.0 software and an installed chromatographic capillary column with the following parameters: length – 100 m, diameter – 0.25 mm, phase – non-polar, DB-1, dimethylpolysiloxane. The evaporator temperature is 573 K, the detector temperature is the same. To determine the Kovacs retention indices, n-alkanes C_{24} – C_{31} were used as reference values. The determination of retention indices was carried out in isothermal mode at temperatures of 523, 533 and 543 K.

The dependence of retention indices on the number of carbon atoms in dibasic acids was assessed with the aim of using these dependencies to calculate the retention indices of unstudied esters of linear dibasic acids and 3,5-di-tert-butyl-4-hydroxybenzyl alcohol. Sorption enthalpies were calculated and their dependence on retention indices was evaluated.

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1-ETHYL-3-METHYLIMIDAZOLIUM METHANESULFONATE: LOW-TEMPERATURE HEAT CAPACITY AND STANDARD THERMODYNAMIC FUNCTIONS OF FORMATION. PART I

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The scientific literature has accumulated a large amount of data on the physicochemical properties of ionic liquids. To optimize technological processes, as well as expluatation conditions, it is necessary to have data on the thermodynamic properties of these substances. Despite the fact that ionic liquids have been the subject of research for several decades, in the scientific literature and international databases the thermodynamic properties of ionic liquids are presented fragmentarily. The object of this work is 1-ethyl-3-methylimidazolium methanesulfonate (EmimMS). The aim of the work is to determine the low-temperature heat capacity over a wide temperature range and to calculate the standard thermodynamic functions of the EmimMS formation in the crystal and liquid states.

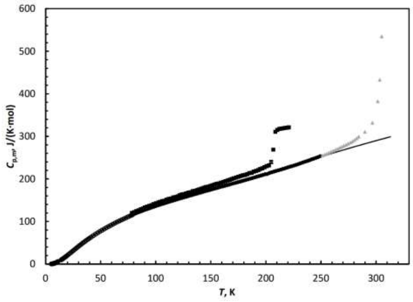

Figure 1. Isobaric molar heat capacity of crystal and glass EmimMS.

The isobaric heat capacity of the crystal and liquid phases of EmimMS was determined in the temperature range from 80 to 380 K by the vacuum adiabatic calorimetry. Two phase transitions were observed: G-type at 203.3±0.5 K and melting at 313.01 ± 0.2 K (Figure 1). Melting parameters were also refined by DSC. At temperatures from 5 to 80 K the heat capacity of EmimMS was assessed by the Kelly method. The temperature dependencies of EmimMS main thermodynamic functions have been determined in the temperature range from 5 to 380 K (isobaric heat capacity $C_{p,m}(T)$, standard entropy $S^0_m(T)$, heat content $H^0(T) - H^0(0)$, Gibbs energy content $G^0(T) - H^0(0)$). In the present study the standard entropies and Gibbs energies of EmimMS formation in the crystal and liquid state at 298.15 K were calculated from the experimental data of adiabatic calorimetry in conjunction with dissolution calorimetry data [1]. Comparison of the obtained thermodynamic characteristics with the literature data was carried out.

[1] L.A. Tiflova, D.A. Kalinyuk , A.I. Druzhinina, *Book of abstracts of XXIII International Conference on Chemical Thermodynamics in Russia,* 2022, 86.

Investigation was supported by the Program “Chemical Thermodynamics and Theoretical Material Science” (AAA-1210313000391) and by the Federal Project "Growth of Advanced Infrastructure for Research and Development in the Russian Federation" of the national project "Science and Universities" (updating of equipment for scientific research).

1-BUTYL-3-METHYLIMIDAZOLIUM METHANESULFONATE: LOW-TEMPERATURE HEAT CAPACITY AND STANDARD THERMODYNAMIC FUNCTIONS OF FORMATION. PART II

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This work is a part of systematic study of the thermodynamic properties of ionic liquids by classical thermochemical methods: low-temperature vacuum adiabatic calorimetry and dissolution calorimetry. The object of this study is 1-butyl-3-methylimidazolium methanesulfonate (BmimMS). The aim of the work is to determine the low-temperature heat capacity over a wide temperature range and to calculate the standard thermodynamic functions of the BmimMS formation in the crystal and liquid states.

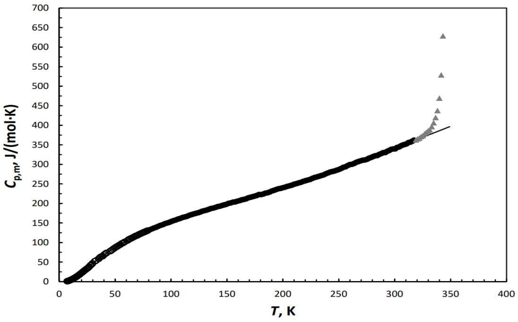

Figure 1. Isobaric molar heat capacity of crystal BmimMS.

The isobaric heat capacity of the crystal and liquid phases of BmimMS was determined in the temperature range from 80 to 380 K by the vacuum adiabatic calorimetry. There are no phase transition exept melting at 349.13 ± 0.2 K on the heat capacity curve of BmimMS (Figure 1). Melting parameters were also refined by DSC. At temperatures from 5 to 80 K the heat capacity of BmimMS was assessed by the Kelly method. The temperature dependencies of BmimMS main thermodynamic functions have been determined in the temperature range from 5 to 380 K (isobaric heat capacity $C_{\mathrm{p,m}}(T)$, standard entropy $S^{0}{}_{\mathrm{m}}(T)$, heat content $H^{0}(T) - H^{0}(0)$, Gibbs energy content $G^{0}(T) - H^{0}(0)$). The BmimMS enthalpy of formation at 298.15 K was previously determined by the dissolution calorimetry [1]. In the present study the standard entropies and Gibbs energies of BmimMS formation in the crystal and liquid state at 298.15 K were calculated from the experimental data of adiabatic calorimetry in conjunction with dissolution calorimetry data. Comparison of the obtained thermodynamic characteristics with the literature data was carried out.

[1] L.A. Tiflova, D.A. Kalinyuk , A.I. Druzhinina, *Book of abstracts of XXIII International Conference on Chemical Thermodynamics in Russia,* 2022, 86.

Investigation was supported by the Program “Chemical Thermodynamics and Theoretical Material Science” (AAA-1210313000391) and by the Federal Project "Growth of Advanced Infrastructure for Research and Development in the Russian Federation" of the national project "Science and Universities" (updating of equipment for scientific research).

CALCULATION OF THE CHEMICAL POTENTIAL OF WATER IN THE LIQUID FILM ON THE SPHERICAL HYDROPHILIC NANOPARTICLE

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Methods of molecular modelling, such as molecular dynamics (MD) and Monte Carlo (MC) methods, can be successfully applied to tackle various scientific problems including the studies of the properties of droplets, liquid films and bubbles on the surfaces having different spatial structure, curvature, chemical composition, etc. One of the most important properties of the surfaces is their wettability, since the ability to regulate it opens up ample opportunities for practical applications. In this work we carried out hybrid MD/MC simulations of the nucleation of all-atom water on a spherical nanoparticle with the hydrophilic surface which consisted of approximately 900 Ag atoms. We considered different number of water molecules around the particle which varied from 400 to 5000. In order to get the chemical potential of the water molecule we used the expanded ensemble method [1,2] together with the Wang-Landau algorithm [3] within the molecular dynamics simulation (this approach was implemented in the MDynaMix v.5.2.8 package [4,5] which we employed). The radial distribution functions of the water molecules with respect to the center of mass of the nanoparticle could be used to determine the thickness of the water film. Thus, the dependence of the chemical potential on the thickness of the water film was obtained. The simulations were carried out in the NVT statistical ensemble. The linear size of the simulation box L was equal to 120 Å, and the temperature of the system T was equal to 293 K. Double time step algorithm [7] was used in the simulations with the long time step of 2 fs and the short time step of 0.2 fs. Nosé thermostat was used for the temperature control [8]. The cut-off radius for the Lennard-Jones interactions [9] R_{cut} was equal to 20 Å. We used Ewald summation [10] to treat the long-range Coulomb interactions. The Lennard-Jones parameters for the Ag atoms were taken from [6]: $M = 107.8682$ a.e.m, $\sigma_{\mathrm{Ag}} = 2.955$ Å, $\varepsilon_{\mathrm{Ag}} = 19.079$ kJ/mol. The TIPS3P water model was used in the simulations, i.e. the TIP3P model with the non-zero Lennard-Jones parameters for hydrogen atoms: $\sigma_{\mathrm{H}} = 0.4$ Å, $\varepsilon_{\mathrm{H}} = 0.192$ kJ/mol.

This work was initiated by Prof. Alexander K. Shchekin who to our great sadness had passed away in July 2023.

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This work was supported by the Russian Science Foundation under grant no. 22-13-00151, https://rscf.ru/en/project/22-13-00151/.

COMPARISON OF THE REDLICH-KISTER-MUGGIANU AND ASSOCIATED SOLUTION MODELS FOR DESCRIBING MELTS WITH STRONG SHORT-RANGE ORDERING IN THE SYSTEMS (Ag, In)–Pd–Sn

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Thermodynamic modeling plays a significant role in the study of phase diagrams of multicomponent systems. The quality of predicting thermodynamic properties and phase equilibria in multicomponent systems depends on the reliability and methods of describing boundary subsystems. The Redlich-Kister-Muggianu (RKM) polynomials is widely used to describe disordered ternary phases. However, thermodynamic modeling of systems with strong short-range order (SRO) using the RKM model is often difficult. The literature indicates that other models may be more effective for such systems: the associated solution (AS) model or a modified quasi-physical model.

In this work, using the example of ternary systems (Ag, In)–Pd–Sn with strong short-range order, the effectiveness of the RKM and AS models in describing the properties of the melt was compared.

The thermodynamic properties of the melt of ternary systems (Ag, In)–Pd–Sn were calculated using the RKM and AS models. The corresponding thermodynamic descriptions of the Pd-Sn binary were accepted from [1]. It is found that without ternary interactions in both ternary systems, the associated solutions model reproduces the literature experimental data on component activities and enthalpy of formation much better. Figure 1 shows a comparison of the calculated enthalpies of melt formation with experimental data [2, 3].

In the In–Pd–Sn, the RKM model showed comparable results with ternary interactions, but it should be noted that the ternary parameters had high modulus values. In the case of the Ag–Pd–Sn system, using the RKM model with ternary interactions, it was not possible to obtain a consistent description of the thermodynamic properties of the melt and phase boundaries, and spurious miscibility gaps appeared.

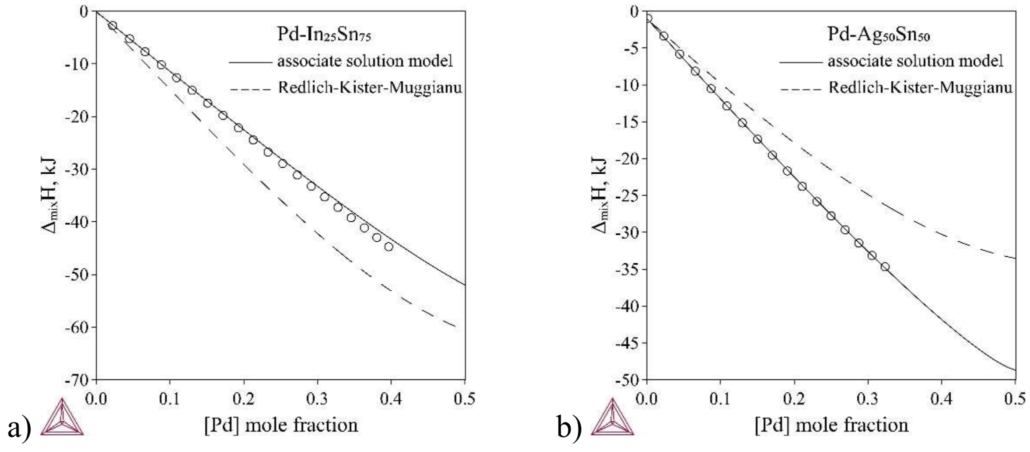

Figure 1. Comparison of the calculated enthalpies of melt formation of the In–Pd–Sn (a) and Ag–Pd–Sn (b) system with experimental data [2, 3].

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COARSE-GRAIN DESCRIPTION OF FLUID INTERFACES APPLYING MULTILAYER QUASICHEMICAL MODEL

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Recently developed Multilayer Quasichemical Model (MQuM) [1] of a nonuniform fluid mixture provides a remarkably detailed structural information about the interfaces between phases and mesoscopic aggregates, including the local concentration and orientation of functional groups of the molecules, the chemical bonds of molecular chains and the orientation profiles of the hydrogen bonds. MQuM generalizes the original Smirnova's approach [2] (formulated for r-mer + monomer solution in the vicinity of a flat sold wall), to fluid interfaces, both flat and curved. By taking into account correlations between functional groups, MQuM extends the range of applicability of the widely used lattice models of fluid interfaces to systems with specific interactions.

However, an important limitation of MQuM – the requirement of the equal size of solvent molecules and monomeric units of the chainlike molecules – substantially narrows its applicability because of the size difference in many real systems. A coarse-graining approach that proved very useful in computer simulations is to combine several structural units or even molecules into a single bead, as e.g., in the MARTINI method [3].

The goal of this work is to test a similar method with MQuM, choosing the beads of approximately equal size. For this test, we took interfacial boundaries between water and n-alkanes (oil) in presence of a polyoxyethylene glycol ether surfactants, $H(CH2)_n(OCH2CH2)_mOH$ (C_nE_m), often considered as an architype for nonionic surfactants [3]. As in MARTINI, four water molecules make a single bead, fragments of the hydrocarbon tail and oxyethylene head represent the other beads. We discuss the results of calculation of the mutual solubility of n-alkanes and water, the predicted structure and properties of the interfaces from both the coarse-grained and the original versions of MQuM, and compare our results with experiment and computer simulations.

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For financial support, we thank the Russian Science Foundation, grant 20-13-00038-П.

DIAXIAL COMPLEXES OF Sn(IV)-TETRAARYLPORPHYRIN WITH ROSE BENGAL: LIMINESCENT PROPERTIES AND ANTIBACTERIAL ACTIVITY

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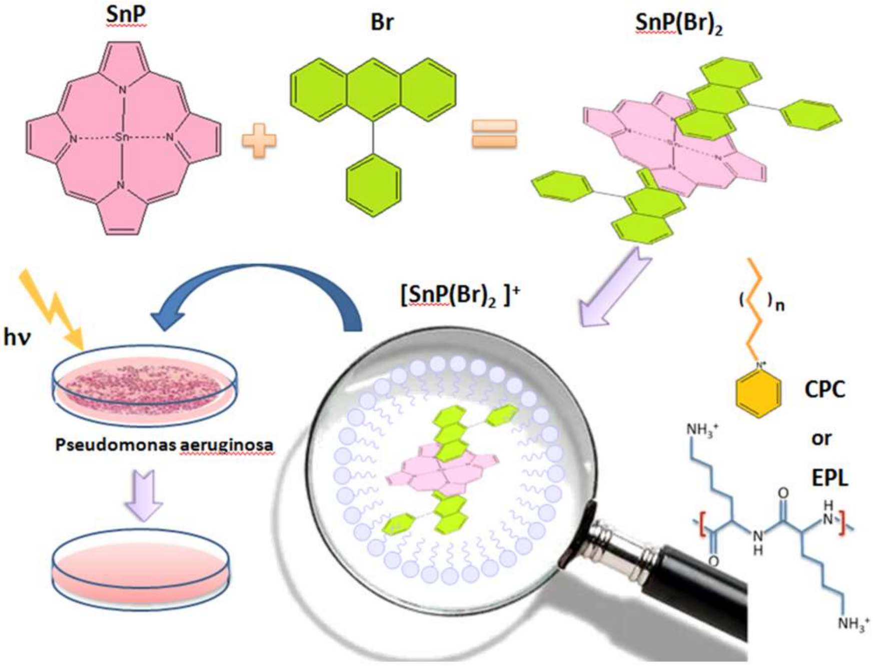
The axial complex (triad) of Sn(IV)-tetraphenylporphyrinsulfonate (**SnP**) with Rose Bengal (**BR**) was obtained where axial binding is realized through the hydroxyl groups of xanthene [**SnP(BR)$_2$**]. Their luminescent properties (fluorescence and ability to generate singlet oxygen at room temperature) in aqueous media with additives of surfactant CPC of various concentrations and ε-poly-L-lysine (EPL) were studied. It was found that the presence in the triad of photoinduced energy transfer from the **BR** fragment to the porphyrin **SnP** fragment and its effectiveness depend on the nature of the medium (surfactant additives). It has been established that the ability of the triad to generate singlet oxygen in D_2O in aqueous and aqueous micellar media is higher than that of its constituent fragments. The dark and photodynamic antibacterial activity of the triad with BR against two microorganisms (Pseudomonas aeruginosa and Staphylococcus aureus) was analyzed.



It has been established that the diaxial complex of the anionic tetra-(4-sulfophenyl)porphyrin Sn(IV) with **BR** has antibacterial activity against both strains. However, in relation to Staphylococcus aureus, the triad showed both light and dark activity, which was stronger than that of **BR**. In relation to Pseudomonas aeruginosa, the xanthene complex of the Sn(IV)-porpyrin exhibits cytoactivity only in the presence of a positively charged polylysine micellar shell and under strong irradiation. As our studies have shown, the micellar shell of CPC has its own high antibacterial activity without irradiation.

FEATURES OF HYDRATION AND COMPLEX FORMATION OF PROTEIN TYROSINE PHOSPHATASE 1B

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Hydration of biomolecules is fundamental process for the functioning of living organisms and underlie most cellular functions. In addition to the fact that hydration is largely responsible for the packing, structural stability, and activity of the proteins themselves, it can also give an essential effect to the stabilization of protein-ligand complexes. Here we present the results of molecular dynamics (MD) study for protein tyrosine phosphatase 1B (PTP1B) in the unbound and ligand-bound states. MD simulations provide a high-resolution view of the motions of biomolecules in the form of continuous trajectories and from it a description of various properties including solvation at atomic or molecular levels.

PTP1B, a cytosolic soluble monomeric enzyme, is a ubiquitous and abundant intracellular enzyme that performs a central role in multiple cellular processes, especially, glucose uptake, body mass regulation, motility, and proliferation. This enzyme is a key player in several human diseases, such as diabetes, obesity, and hematopoietic malignancies, and, thus, for them it is a validated target for drug development and design. However, to date little is known about the hydration of PTP1B and its complexes with ligands.

To give a three-dimensional molecular picture of the hydration of this protein, we applied all-atom MD simulations. To this end, a number of the X-ray crystal structures of PTP1B from Protein Data Bank (PDB) such as ligand-free structure (PDB ID is 2HNP), complexes with compact (PDB ID is 2HB1) and extended (PDB ID is 2QBP) ligands were used. In our contribution, we provide a 3D-analysis for the hydration of unliganded and liganded PTP1B as well as discuss the changes in this process occurring upon the complex formation of protein with inhibitors to understand more about the role of hydration during the binding of a ligand to a target molecule.

This work was supported by the Russian Science Foundation (project No. 22-23-00184, https://rscf.ru/en/project/22-23-00184/ (accessed on 15 December 2021).

THERMODYNAMIC PROPERTIES IN THE Cs_2O-SrO-Al_2O_3-SiO_2 SYSTEM STUDIED BY THE KNUDSEN EFFUSION MASS SPECTROMETRIC METHOD

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Vaporization of cesium and strontium compounds from the core material during severe accidents at nuclear power stations may lead to hazardous radioactive pollution of the environment [1]. For better understanding of high temperature behavior of multicomponent core material, the model Cs_2O-SrO-Al_2O_3-SiO_2 system was considered in the present study since alumino-silicate matrices were mentioned as potential candidates for reliable waste forms for cesium and strontium [2].

In the present study, the vaporization processes and thermodynamic properties of the Cs_2O-SrO-Al_2O_3-SiO_2 system were studied by the Knudsen effusion mass spectrometric (KEMS) method [3]. The samples in the system under consideration were synthesized by the sol-gel method based on Cs_2CO_3, $SrCO_3$, $Al(NO_3)_3 \bullet 9H_2O$, and tetraethoxysilane $(C_2H_5O)_4Si$ as initial components involving nitric acid with the maximum annealing temperature of 1073 K for 622 hours. The samples obtained were characterized by X-ray phase analysis, electron probe microanalysis, differential thermal analysis, and X-ray fluorescence analysis. Identification of the structure as well as phase and chemical compositions of the samples of the Cs_2O-SrO-Al_2O_3-SiO_2 system allowed the KEMS study to be carried out using an MS-1301 mass spectrometer at an ionizing voltage of 30 V from a single tungsten effusion cell.

The vaporization of the samples in the Cs_2O-SrO-Al_2O_3-SiO_2 system was observed at temperatures above 900 K. The main vapor species over the samples were Cs and O_2, leading to selective removal of Cs_2O from the samples. The vaporization of the samples without Cs_2O was found at temperatures above 1800 K, with the main vapor species being Sr, SiO, and O_2. The temperature dependences of the partial pressures of the vapor species over the samples under study were obtained by the KEMS method. These data enabled the partial vaporization enthalpies of Cs_2O as well as mass losses of the samples to be determined. The data obtained were also used to derive the temperature dependences of the component activities and calculate partial molar enthalpies of mixing in the Cs_2O-SrO-Al_2O_3-SiO_2 system. Negative deviations from the ideal behavior were established in the system under study at the temperatures 1000, 1100, and 1200 K. It was shown that introduction of SrO in the Cs_2O-Al_2O_3-SiO_2 system led to decrease in the Cs_2O activity coefficients. As for the influence of Al_2O_3 and SiO_2, the minimum values of the Cs_2O activity coefficients were observed in the samples with the equimolar content of Al_2O_3 and SiO_2, showing the concentration ranges with the optimal thermal stability.

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COMPUTER SIMULATION OF AEROGEL IMPREGNATION WITH MEFENAMIC ACID IN A SUPERCRITICAL CO_2 ENVIRONMENT

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Aerogels possess a number of unique properties that make them highly attractive for use in various fields: very low density, low coefficients of thermal conductivity, electrical conductivity, light refraction, and high porosity. There are several types of aerogels that differ in composition and properties. One of the most common types is silica aerogels, which are manufactured based on silicon oxide. The advanced internal structure of aerogels allows them to be used as matrices-carriers for various active substances, such as pharmaceutical compounds. Thus, aerogels can become a fundamental component for obtaining new forms of pharmaceutical compounds. For successful loading inside the aerogel matrix, the substance must be soluble in a supercritical fluid. Mefenamic acid belongs to the group of non-steroidal anti-inflammatory drugs from the fenamate group, which has analgesic, anti-inflammatory, and antipyretic effects. The study conducted molecular dynamics modeling of impregnating silica aerogels with mefenamic acid in a supercritical carbon dioxide environment. The modeling was conducted at different temperatures and densities of carbon dioxide, equal to 1.1 times the critical density of CO_2. The metadynamics method was applied for calculations of free energy of conformational transitions. It allows for a correct calculation of the free energy of conformational transitions between states separated by high energy barriers. The results of the conducted calculations are discussed in the report.

The work was carried out with the financial support of the Russian Science Foundation grant No. 22-13-00257.

POLYMER COMPOSITE MEMBRANES BASED ON meta-POLYBENZIMIDAZOLE AND DIETHYLAMMONIUM MESYLATE PROTIC IONIC LIQUID

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For a long time, the attention of researchers has been attracted by proton ionic liquids (PILs), which are endowed with such unique properties as aprotic ones, exactly low vapor pressure, high thermal stability, low flammability, nontoxicity. Their structure contains an "active" (mobile) proton, which makes them ideal electrolytes for fuel cells with a proton exchange membrane. The incorporation of ionic liquids into polymer matrices has become a very promising approach to improving the ionic conductivity of membranes. They can act at the same time as a plasticizer, weakening the interaction between polymer chains, and as an ion-supplying material. The variety of polymers used as a matrix and the limitless amount of ILs obtained by varying the cation-anion composition makes it possible to obtain polymer electrolytes with a wide range of desired characteristics.

Here we present the thermal (phase transitions and decomposition temperatures) and electrochemical (specific electrical conductivity) properties of membranes based on poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (PBI) doped with diethylammonium mesylate (DEA/MsO), a protic ionic liquid, at various molar ratios of the components (2/2, 3/2, 4/2, 5/2).

It was found that all the membranes demonstrate similar thermal behavior. According to TG analysis, the first weight loss (~8%) occurs at temperatures up to 100 °C, which may be due to the removal of residual solvent. In the temperature range of 250-270 ° C the membrane decomposition starts. Obviously, the thermal stability of the membranes is determined by the decomposition temperature of pure DEA/MsO (T_{onset} = 254 °C).

The melting temperature of pure DEA/MsO is equal to 45.5°C. In contrast to that no phase transitions are observed on DSC thermograms of the membranes under investigation in the range from -100 to 200 °C.

The membrane conductivity increases both with temperature and ionic liquid content increasing and reaches 3.8 $mSm\cdot cm^{-1}$ for the membrane with n(IL)/n(PBI)=5/2 at 150 °C. The addition of SiO_2 leads to an increase in electrical conductivity. For example, the conductivity of the same membrane with 20% of SiO_2 becomes almost twice as much (6.3 $mSm\cdot cm^{-1}$ at 150 °C).

PHASE AND CHEMICAL EQUILIBRIA IN THE SYSTEM Ca – PHOSPHATE – POLYASPARTIC ACID – H_2O UNDER THE DIRECT CURRENT

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The purpose of the study is to perform a mathematical modelling of the phase transitions of hydroxyapatite under the influence of direct electric current in order to evaluate its stimulating effect on osteogenesis.

The model was an electrolytic cell with two graphite electrodes. The chemical equilibria were modelled in a 0.89% sodium chloride solution mixed with calcium ions and phosphate ions with different total concentrations of calcium and phosphorus equal to each other (0.0001 M, 0.0005 M, 0.001 M, and 0.005M), and the same solution with the presence of 0.001 M polyaspartic acid. The transmission of electric current up to 100 mA for 60 s was considered.

In the entire range of pH values (4–13), the amorphous calcium phosphate was the least stable. It was found that at pH above 6.5 in the entire range of the studied concentrations of generated hydroxide ions, hydroxyapatite was the most stable phase under the action of electric current. At the same time, in the absence of such an impact, the formation of hydroxyapatite occurs within pH=9. From a thermodynamic point of view, amorphous calcium phosphate is both the most soluble and the least stable of all calcium phosphates. However, the generally accepted opinion is that it participates in the mechanism of osteogenesis as the initial sediment phase stabilized by high molecular weight peptides.

In the presence of polyaspartic acid the solubilities of all forms of calcium phosphates slightly increase due to formation of the calcium and aspartic acid chelates. However, it does not have a significant effect on their stability, which also confirms the assumption about the predominance of the kinetic factor in the formation of amorphous phosphate during osteogenesis.

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VAPORIZATION AND THERMODYNAMIC PROPERTIES IN THE Cs_2O-Al_2O_3-SiO_2 AND SrO-Al_2O_3-SiO_2 SYSTEMS STUDIED AT HIGH TEMPERATURES

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The vaporization processes and thermodynamic properties in the Cs_2O-Al_2O_3-SiO_2 and SrO-Al_2O_3-SiO_2 systems were studied by the high temperature mass spectrometric method. The samples in the system under consideration were synthesized by the sol-gel method. The samples obtained were characterized by X-ray phase analysis. This study was performed using the MS-1301 mass spectrometer at an ionizing voltage of 25 V. Samples of Cs_2O-Al_2O_3-SiO_2 system were evaporated from a single Knudsen effusion cell heated by resistance furnace. The temperature was measured with a platinum-platinum-rhodium thermocouple. The samples of the SrO-Al_2O_3-SiO_2 system were evaporated from twin effusion cell heated by electron bombardment. In one of the compartments of the cell, the studied sample was loaded, and in the second, comparative, individual SrO or SiO_2. In that case the temperature was measured by an optical pyrometer. Instrument calibration was performed using the calcium fluoride.

The vaporization of the samples in the Cs_2O-Al_2O_3-SiO_2 system was observed at temperatures above 750-900 K, depending on the Cs_2O content. The main vapor species over the samples were Cs and O_2, leading to selective removal of Cs_2O from the samples. The vaporization of the samples without Cs_2O was observed at temperatures above 1800 K, with the main vapor species being SiO, Al, AlO, Al_2O and O. The temperature dependences of the partial pressures of the atomic cesium over the samples under study allowed us to determine the activity of cesium oxide and the chemical potential of Cs_2O and excess Gibbs energies. Negative deviations from the ideal behavior were illustrated in the system under study at the temperature range 750-900 K.

A characteristic feature of the SrO-Al_2O_3-SiO_2 system is the rather different volatility of the constituent components. The most volatile one is silicon dioxide, the least volatile component is aluminum oxide. During isothermal aging, the composition of the condensed phase of the system under study is constantly depleted of silicon and strontium oxides, and enriched with aluminum oxide.

The obtained values of the activities of strontium oxide in the studied samples indicate the presence of a negative deviation from ideality in the temperature range 1950-2100 K. In the same temperature range, the values of SiO_2 activity are close to the ideal state. It was found that in samples containing 30 SrO:50 Al_2O_3:20 SiO_2 and 30 SrO:20 Al_2O_3:50 SiO_2 (mol. %), with a relative increase in the concentration of SiO_2 and a decrease in the concentration of Al_2O_3 in the sample, the value of the SrO activity decreases. This is due to the fact that the difference in acid-base properties of oxides in the SrO-SiO_2 system is greater than in the SrO-Al_2O_3 system. However, the lowest the SrO activity is typical for a sample containing 33 SrO:33 Al_2O_3:33 SiO_2 (mol. %).

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EFFECT OF COAGULATION BATH HARSHNESS ON STRUCTURE FORMATION AND PROPERTIES OF POLIVINYLIDENE FLUORIDE MEMBRANES PREPARED VIA NONSOLVENT INDUCED PHASE SEPARATION

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As a sustainable approach, the membrane separation is playing an increasingly important role for the processing and recovery of target compounds from various gas and liquid streams due to its lower energy cost, footprint, and flexibility in operation. Polyvinylidene fluoride is one of the most widely used polymers for membrane preparation nowadays. The polyvinylidene fluoride membranes are mainly obtained via phase inversion processes, in particular nonsolvent induced phase separation. In recent years more and more studies devoted to elucidation of mechanism of structure formation appear. However this problem remains controversial. In the present study we propose a new look at the mechanism of structure formation during nonsolvent induced phase separation based on analysis of the previously plotted by us experimental phase diagram for the polyvinylidene fluoride – dimethyl acetamide – water mixture [1]. In particular, we report the effect of the precipitation bath harshness on the morphology, crystalline structure, physico-mechanical, and transport properties of the membranes. Harshness of precipitation bath was controlled by addition of solvent to the nonsolvent. Detailed analysis of the scanning electron microscopy images of both surfaces and cross-sections of the prepared membranes enabled us to explain the observed transformations of the structure formation mechanisms. It was shown that an increase in dimethyl acetamide concentration in the precipitation bath leads to the transformation of membrane morphology from the asymmetric, which is standard for the ultrafiltration membranes and composed of a selective skin layer, a layer with finger-like pores and a layer with a sponge-like structure to a more symmetric structure that does not contain finger-like pores. It is established that the transcrystalline structure is formed in the surface layer of the membranes, while, in the bulk of the membrane, the spherulites with different morphologies can be formed depending on the parameters of the membrane preparation process. It is established that a decrease in the precipitation bath's harshness leads to an increase in the membrane transport properties (mean pore size from ~60 to ~150 nm and permeance from ~2.8 to ~8 L m^{-2} h^{-1} bar^{-1}) while the mechanical properties of the membranes pass through a maximum (tensile strength changes from ~9 to ~11 and to 6 MPa, while elongation at break increases from ~140 to ~190% before dropping to values as low as 35%). Based on analysis of the obtained results recommendations are given regarding optimal composition of precipitation bath for preparation of ultrafiltration polyvinylidene fluoride membranes. More detailed information can be found in [2].

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STUDY OF THE INFLUENCE OF TEMPERATURE ON THE CONFORMATIONAL EQUILIBRIA OF LIDOCAINE IN SUPERCRITICAL CARBON DIOXIDE USING 2D NOESY

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Solubility in water is essential in determining the bioavailability of many drug compounds. However, the drug must also have a certain degree of hydrophobicity to pass through biological membranes. The balance between hydrophilicity and hydrophobicity of API (active pharmaceutical ingredients) is essential for the effectiveness of a drug compound. Poorly soluble APIs, which are part of dosage forms, also require modification. Micronization methods are a reliable way to modify APIs to increase their solubility in water by increasing the specific surface area of micronized particles. Micronization using SCF technologies is the most actively developed among the various existing methods. SCF can produce the most petite particle sizes compared to other methods while having the properties of both a gas (diffusion and compressibility) and a liquid (density and dissolving capability). Supercritical carbon dioxide (scCO2) is the most accessible solvent due to its critical point state parameters (T = 31 °C, P = 7.38 MPa). In this study, the possible conformers of lidocaine in scCO2 were determined for the first time. The study was conducted within three isobars (10, 20, and 30 MPa) and 35, 50, and 70 °C temperatures.

The earlier quantum-chemical calculations revealed two conformers groups, Cis- and Trans- groups. The study's results indicate that the proportion of Cis-conformers and Trans-conformers present in a substance depends on the temperature. As the temperature increases, the proportion of Cis-conformers also increases, and the ratio of Trans-conformers increases as the temperature decreases. For instance, on the 10 MPa isobar, the Trans- / Cis-conformers ratio changes from 99.4 % / 0.6 % to 88.9 % / 11.1 % when the temperature increases from 35 °C to 70 °C. On the 20 MPa isobar, the distribution of conformers changes from 53.3 % / 46.7 % to 95.6 % / 4.4 % at the same temperatures. Similarly, on the 30 MPa isobar, the corresponding values are 4.8 % / 95.2 % and 46.5 % / 53.5 % (Figure 1).

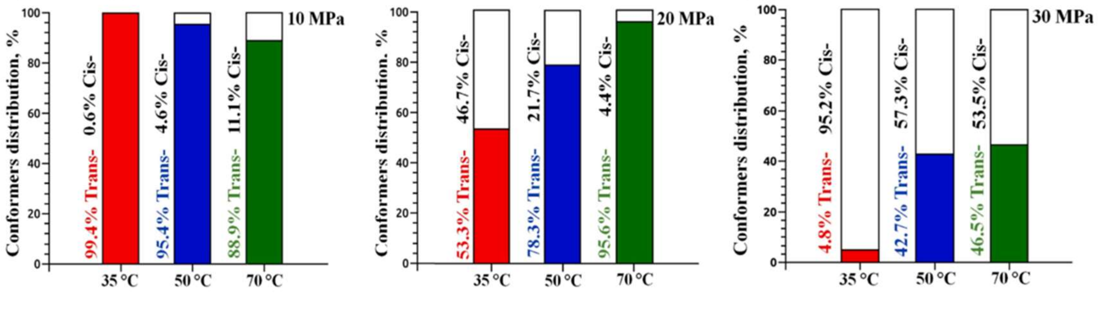

Figure 1. Distribution diagrams of fractions of conformer groups of the lidocaine molecule in $scCO_2$ at pressures of 10 MPa, 20 MPa and 30 MPa and temperatures of 35, 50 and 70 °C

It is intriguing how the proportions of conformer groups vary with temperature and this knowledge could be beneficial for micronizing different compounds using supercritical fluid technologies.

The NMR spectroscopy experiment was performed using the molecular fluid spectroscopy facility (http://www.ckp-rf.ru/usu/503933) of G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences (ISC RAS) (Russia).

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INVESTIGATION OF THE SELECTIVE PROPERTIES OF IONIC LIQUIDS

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The selective properties of ionic liquids (IL) for the separation of organic solvents mixtures have been studied by gas-liquid chromatography (GLC). It is proposed to evaluate the selective effect of the tested agents (S_{12}^{∞}) by the retention times of substances in the chromatographic column [1]:

$$S_{12}^{\infty} = \frac{t_{R2}}{t_{R1}}$$

t_{R1}, t_{R2} – adjusted retention times of separable components 1, 2.

IL's selectivity S_{12}^{∞} as extractive agents was evaluated for azeotropic mixtures containing methanol (M), tetrahydrofuran (THF), acetonitrile (ACN), and chloroform (CLF). Usually, industrial extractive agents are used to separate them [2, 3]. The tested ILs contain chloride anion, the cations are [1-ethyl-3mim], [1-buthyl-3mim], [1-buthyl-2,3-dmim].

Standard approaches to analytical GLC procedures for preparing sorbents and columns and techniques for measuring the retention parameters of components were used [1]. ILs were applied as the liquid stationary phase in quantities 2.5, 5, 7.5, and 10 mass. % of substrate's weight (Chromosorb W45/60 mesh).

The influence of ionic liquids on the separation of azeotropic pairs is analyzed. The greatest values S_{12}^{∞} selectivity for the THF (1) – ACN (2) is fixed for [1-ethyl-3mim][Cl]: 2.5 %, $S_{12}^{\infty} \approx 1.7$; 10%, $S_{12}^{\infty} \approx 3.8$. The selectivity for the THF (1) – CLF (2) is the same for [1-buthyl-3mim][Cl], [1-buthyl-2,3-dmim][Cl]: 2.5 %, $S_{12}^{\infty} \approx 2.4$; 10%, $S_{12}^{\infty} \approx 5.5$. The greatest increase S_{12}^{∞} of [1-buthyl-2,3-dmim][Cl] was recorded for THF (1) – M (2): 2.5 %, $S_{12}^{\infty} \approx 4.5$; 10%, $S_{12}^{\infty} \approx 14$. ILs exhibit the same influence in relation to azeotropic pairs. The retention times of THF (1) in the chromatographic column are always lower, consequently, in the presence of ILs isolation of THF is predicted.

The ILs considered in this work are not recommended for the separation of CLF – M and ACN – CLF mixtures due to low selectivities. [1-Ethyl-3mim][Cl] and [1-buthyl-3mim][Cl] exhibit low selectivity for ACN (1) – M (2): 10%, $S_{12}^{\infty} < 3.5$. So it is recommended to use [1-buthyl-2,3-dmim][Cl]: 10%, $S_{12}^{\infty} \approx 4.5$.

The ratio of S_{12}^{∞} values for a fixed ILs concentration is maintained only for the THF – CLF. The dependencies of selectivity on concentration for different ILs are intersects for other pairs of components. Nevertheless, ehe increase in the concentration of IL and its selectivity is unidirectional for all azeotropic pairs.

It is recommended to use [1-buthyl-3mim][Cl] for the separation of THF – CLF, [1-ethyl-3mim][Cl] for THF – ACN, and [1-buthyl-2,3-dmim][Cl] for THF – M and ACN – M.

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DSC STUDY OF PHASE TRANSITIONS IN ETHYL CELLULOSE/BENTONITE POLYMER COMPOSITES

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The most important task of modern polymer-materials science is to develop and improve the methods of synthesis of new multifunctional materials and investigate their physicochemical properties for the purpose of practical use in various fields. Modification of a polymer matrix by introducing fillers is an effective way to obtain such materials. Such composites can exhibit improved mechanical, electric, and antimicrobial characteristics, and they can be applied in many industries, biochemistry, and medicine as sensors, adsorbents, catalysts, and membranes. However, the effective use them often requires that the peculiarities of processing and operation at elevated temperatures be taken into account. Therefore, the study of the thermal behaviors of polymer composites is relevant to their practical use.

In the present work, we prepared samples of ethyl cellulose/bentonite (EC/bent) composite films with a clay mineral concentration ranging from 0 to 7 wt %. The thermal behavior of the prepared materials, as well as the original EC powder was studied by differential scanning calorimetry (DSC) within a range of temperatures from 25 to 210°C. In all recorded curves (Figure), inflection points were observed that corresponded to glass transition temperatures (T_g), as well as endothermic peaks corresponding to melting (T_m).

It was found that the synthesized film composites were characterized by lower temperatures of glass transition and melting compared to that for powdered EC (Table). We showed that regulation of thermal behaviors of composites is possible by modifying the polymer with a layered silicate that can lead to the expansion of the areas of application of the material.

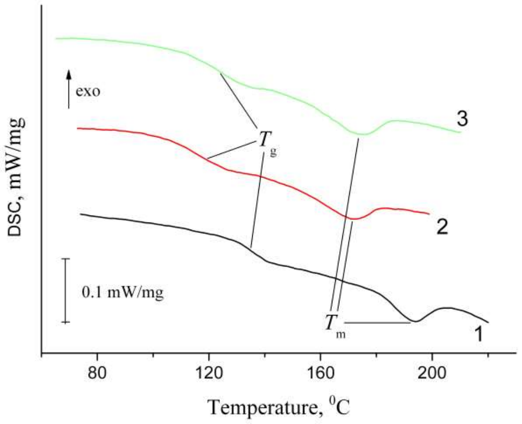

Figure. DSC curves: *1* - EC powder; *2* - EC film; 3 – EC/bent(1%) composite film

Table. Characteristic temperatures of phase transitions for EC/bent composites with different filler concentrations

Concentration of bentonite, wt %	T_g, ^{0}C	T_m, ^{0}C
0	114.2	172.2
1.0	125.0	175.8
3.0	127.5	176.3
7.0	123.6	174.1
EC powder	134.7	194.1

The data obtained should be taken into account when calculating the thermal operating conditions of products based on ethyl cellulose.

THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA OF THE CITRIC ACID – OXALIC ACID – WATER SYSTEM

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The water solutions of citric and oxalic acid widely used in various fields of chemical production [1]. The desulphurisation process based on citrate buffer solution seems to be the most promising renewable process [2] and the oxalate process has a great potential to replace many existing metal recovery processes using inorganic acids such as sulphuric, hydrochloric and nitric acids [3]. To thermodynamic modeling of systems containing oxalic and citric acid, it is necessary to have the thermodynamic properties of systems of smaller dimensions.

Thermodynamic properties and liquid-solid phase equilibria of the citric acid – water [4, 5] and oxalic acid – water [6, 7] systems have been investigated in a wide temperature range. Information on thermodynamic properties and phase equilibria in the citric acid – oxalic acid – water system has not been found in the literature.

The aim of the present work is to obtain a set of experimental data on thermodynamic properties and phase equilibria in the citric acid – oxalic acid – water system, which can be used in further construction of the thermodynamic models of the reciprocal citrate oxalate systems.

Phase equilibria in the citric acid – oxalic acid – water system were investigated at 298.15 K by isothermal dissolution method. In the course of work, initial heterogeneous mixtures of oxalic and citric acids and water were prepared. The obtained mixtures were used for further studies under different holding times. After incubation of the prepared mixtures under the specified conditions, a part of the solution was separated to analyze the aqueous phase, the precipitate was taken from the mother solution using the vacuum filtration method.

The phase composition of the precipitates was analyzed by X-ray phase analysis (XRD). The concentrations of components in saturated solutions above the precipitate were determined by ion chromatography and potentiometric titration methods. During work the acidity of liquid phases was measured using a pH-meter.

Isothermal cross section of phase diagram of the citric acid – oxalic acid – water system was constructed at 298.15 K using the data obtained in the work.

Liquid-vapor equilibria of the citric acid – oxalic acid – water system were studied in the work by dew point and static vapor pressure methods at different temperature.

The density of solutions of the citric acid – oxalic acid – water system at 288.15, 298.15 and 308.15 K was measured during the work.

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MOLECULAR DYNAMICS SIMULATION OF ELECTROLYTES UNDER CONDITIONS OF CONFINED GEOMETRY OF NANOPORES

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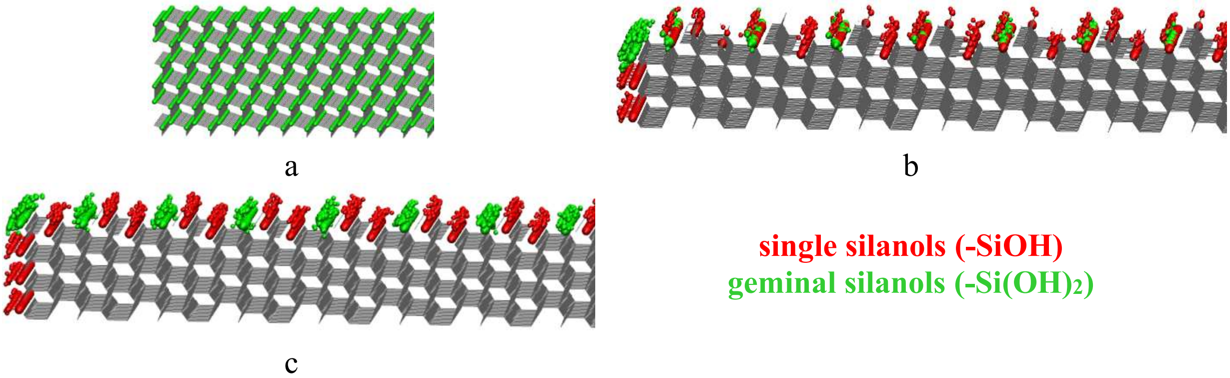
The study of water and aqueous electrolytes confined in nano-scale environments is crucial for various applications, such as in biological systems (enzymes, ion channels), nanofluidic device design, and adsorption/separation processes.

This research focuses on investigating the structural and transport properties of water and aqueous electrolytes within nanopores using molecular dynamics simulation. Specifically, we aim to analyze how the behavior of water and aqueous electrolytes changes based on the slit-pore width and functionalization (with hydroxyl density variations of 0, ~2, and ~6 OH/nm^2) of the β-cristobalite (111) surface. This surface can accommodate both single silanols (Si-OH) and geminal silanols (Si-(OH)$_2$), as observed on amorphous silica surfaces experimentally.



a b c

Figure 1. β-cristobalite (111) surfaces: Non-hydroxylated surface with bridging -O-Si-O- bonds (a), hydroxylated surface with a density of ~ 2.7 OH/nm^2(b) and ~ 6.3 OH/nm^2 (c)

Classical molecular dynamics simulations were conducted using Gromacs 2019.6, applying the NVT ensemble with a temperature of 298 K controlled using the Nose–Hoover thermostat. Long-range interactions were managed using Particle Mesh Ewald (PME) summations, while the SPC/E model described water interactions. Slit pores were created from slabs featuring three different hydroxyl densities.

In examining nano-confined water systems, some level of molecular ordering was detected. This ordering may impact the behavior of water and aqueous electrolyte compared to bulk phase. The density distribution of water and electrolytes between solid walls was analyzed to gain insights into liquid structure and outer layer formation near the interface, based on pore width and surface functionalization. The radial distribution function g(r) provided details on water structure near the silica nanopore surface, including investigations into hydrogen bonding interactions between water molecules and pore surface hydroxyls.

The financial support of the Russian Science Foundation (Grant No. 24-11-00096). The calculations were performed on the supercomputer facilities provided by NRU HSE.

THERMODYNAMIC PROPERTIES OF CeO_2-Gd_2O_3 SYSTEM

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In recent decades, research on ceria and its derivatives has shown their suitability for diverse industrial applications due to their inertness and thermal stability up to 1500°C [1]. Rare earth-doped ceria has been the subject of thorough research as an electrolyte for solid oxide fuel cells (SOFC) due to its exceptional ionic conductivity, which can vary depending on the type and quantity of dopant [2]. Specifically, introduction of Gd^{3+} into the Ce^{4+} sites of the CeO_2 lattice creates oxygen vacancies which are responsible for the high oxygen conductivity at temperatures above 500°C. Gd-doped ceria (GDC) has demonstrated significantly superior performance compared to the frequently utilized Y-stabilized zirconia (YSZ) [3]. Elevated temperatures during the process of synthesis and application could potentially result in the selective evaporation of the constituent components within the examined system. This circumstance has prompted the current exploration of the vaporization processes and thermodynamic properties of the CeO_2-Gd_2O_3 system.

$Ce_{1-x}Gd_xO_{2-x/2}$ ($x = 0.1$ to 0.9 at 0.1 intervals) ceramics were obtained in this study via solid-state synthesis. Phase compositions of the samples after synthesis were confirmed by XRD analysis. The vaporization processes and thermodynamic properties of CeO_2-Gd_2O_3 system were studied by the Knudsen effusion mass spectrometry method. Investigation has been done using MS-1301 mass spectrometer at the ionization energy 30 eV. Vaporization of the samples under consideration was carried out using twin tungsten effusion sell heated by electron bombardment. Temperature was measured by optical pyrometer EOP-66 with the accuracy ±5 K over the temperature range 1900-2500 K

In the mass spectra over CeO_2-Gd_2O_3 in the temperature range 1900-2500 K ions CeO_2^+, CeO^+, Gd^+, GdO^+ were detected. The vapor over the samples in this temperature range consists of CeO_2, CeO, O, Gd and GdO species.

The partial pressures were obtained by ion current comparison method. Thermodynamic activities of CeO_2 and Gd_2O_3 in the samples were obtained using both differential mass spectrometry method and the method suggested by Belton and Fruehan [3], which is based on the Gibbs-Duhem relation.

In the research conducted, it was revealed that CeO_2-Gd_2O_3 system exhibits a negative deviation from an ideal solution.

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ESTIMATION OF THERMAL PROPERTIES OF ALKYLAMMONIUM HYDROGEN SULFATES USING QUANTUM CHEMICAL DESCRIPTORS

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In recent decades, establishing qualitative and quantitative structure–property correlations for protic ionic liquids has become an urgent research direction. The reason for this is obvious: the use of computational methods makes it possible to noticeably reduce the amount of experimental work and significantly decrease material costs for the purposeful synthesis of ionic liquids with the desired properties.

This work analyzes and summarizes data on the structures and properties of R_nNH_{4-n} alkylammonium cations (n = 1–3, R = Me, Et, Pr, Bu) and the ionic pairs formed by them with the hydrogen sulfate anion. All quantum-chemical calculations were carried out using the DFT/B3LYP-GD3/6-31++G(d,p) methodology with the Gaussian 16 software package. The charge distribution of electrostatic potential within ions was used to identify the most probable sites of hydrogen bonding between the cation and the anion. The natural bond orbitals (NBO) method and the quantum theory of atoms in molecules (QTAIM) were performed to study the properties of hydrogen bonds in the ionic pairs. The results indicate that the ionic pairs containing the tertiary ammonium cation have the strongest hydrogen bonds among all the ionic pairs studied. However, the energy values of ion-ion interactions show a greater overall contribution from hydrogen bonds as the number of hydrogen atoms in the cation amino group increases. The strength of the ion-ion interaction is mainly determined by the basicity (proton affinity) of the initial amines.

Multi-parameter regression equations were developed to estimate the decomposition and melting temperatures of 15 studied alkylammonium hydrogen sulfates using quantum chemical descriptors of the cations and ionic pairs. The thermal properties of the liquids were taken from literature sources [1–4]. The regression models obtained show very good performance, with a coefficient of determination close to one, providing a precise fit to the experimental data set. These equations can be used as a basis for indicative predictions of the thermal properties of new alkylammonium hydrogen sulfates, with a view to their synthesis and the possible further application as dopants in polymer membranes for fuel cells.

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PREDICTING THE VISCOSITY OF DEEP EUTECTIC SOLVENTS USING MACHINE LEARNING METHODS

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In recent years, there has been a significant rise in the focus on green technology and the development of safer, more efficient, and environmentally friendly processes. This has led to a surge in publications emphasizing eco-friendly engineering principles, particularly in relation to the use of solvents that are both safe for humans and the environment. Deep eutectic solvents (DESs) are anticipated to offer a superior alternative to conventional organic solvents, which have a negative impact on environmental pollution.

These DESs are formed by combining hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD), creating an eutectic system with a lower melting point than any individual component and a lower temperature than an ideal liquid mixture. The viscosity of DESs is crucial for their potential applications and process design. Despite their promising uses, DESs have limitations such as low diffusion coefficients, a slow gas absorption rate, and low electrical conductivity due to their high viscosity. Viscosity is essential for engineering calculations and scaling up DES applications, influencing factors such as equipment size, pump and heat exchanger performance, and the feasibility of mixing, separation, and product utilization.

In this research, regression models were developed to predict the temperature-dependent dynamic viscosity of DESs. A dataset comprising 3440 data points representing 252 unique DESs was used to train machine learning models. The preferred model is built on the CatBoost algorithm with CDK molecular descriptors. The models were evaluated using both random and artificial data partitions, with results indicating that only a rigorous separation of data can accurately showcase the predictive capability of the model. Additionally, it was observed that models developed solely using mixture data outperformed those developed using data that included pure mixture components. The study also introduced an open-access model (http://chem-predictor.isc-ras.ru/ionic/des) designed to facilitate the formulation of new DESs with targeted viscosity values, aiming to promote wider adoption and exploration of these mixtures.

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THERMOCHEMICAL AND IR SPECTRAL STUDY OF THE INTERACTION OF ASYMMETRIC WATER-SOLUBLE PORPHYRINS WITH BLOOD SERUM ALBUMIN

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Sulfophenyl-substituted porphyrins and related compounds are currently attracting the attention of researchers due to their successful use in various high-tech fields of science and technology. They are used as sensors, liquid crystals, semiconductor materials, sensitizers for photodynamic therapy of oncological diseases, fluorescent diagnostic materials, etc. [1-4]. The variety of areas of application of porphyrins is associated primarily with the wide possibilities for their modification, which makes it possible to obtain new multifunctional materials based on porphyrins with predetermined potentially useful practical properties.

The presence of sulfo groups in the composition of porphyrin molecules provides the macroheterocyclic compound with good solubility in aqueous media, and their high fluorescent ability makes them attractive for bioluminescence imaging, use as pathogen photoinactivators or photosensitizers for theranostics. The fluorescence ability of porphyrins significantly depends on their microenvironment, which is especially important when studying biological substances and biosubstrates. On the other hand, porphyrin compounds themselves can significantly affect biopolymers. DSC provides valuable information about structural changes in complexes of biopolymers with porphyrins.

This work is aimed at expanding knowledge about the effect of complexation of water-soluble unsymmetrical macroheterocycles on the properties of serum albumin (BSA), in particular on resistance to thermally induced denaturation. For this purpose, IR spectral and thermochemical studies of BSA and its complexes with monoheteryl-substituted sulfoporphyrins were carried out.

It was established that the process of complex formation of BSA with the studied porphyrins is carried out due to H-bonding of the peripheral SO3 groups of the porphyrin with the amino acid residues of the protein. All studied porphyrins exhibit thermoprotective properties of BSA, increasing the temperature of protein destruction by 9.5 – 11.5 C. Based on the data obtained, a hypothesis has been put forward about the localization of the studied porphyrins in the protein globule between the IB and IIIB subdomains. The information obtained in this work on the thermal resistance of BSA complexes with porphyrins may be of interest for ebullio- and cryobiology, and the food chemical industry.

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DETERMINATION OF THE TYPE OF COMPLEXES OF OLIGONUCLEOTIDES WITH PORPHYRINS BASED ON THE TEMPERATURE DEPENDENCE OF THE HEAT CAPACITY OF SOLUTIONS

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The temperature dependences of the specific heat capacities of solutions of synthetic oligonucleotides poly[d(AT)2], poly[d(GC)2] and their complexes with porphyrins TMPy3P, TMPy4P, PorN, PorS and PorO were measured using differential scanning calorimetry. Porphyrins TMPy3P, TMPy4P differ in the position of the N-methylpyridyl group in the phenyl peripheral substituent of the porphyrin, and PorN, PorO and PorS are tricationic porphyrins containing N-methylbenzimidazole, benzoxazole and benzothiazole residues. The obtained thermochemical data made it possible to analyze the structural and energetic changes in the solution during the complexation of oligonucleotides (NA) with porphyrins and to establish their nature of interaction.

For all nucleic acids, binding to porphyrins leads to a general decrease in the heat capacity of solutions, i.e. Regardless of the type of complexes formed, the system is stabilized. To analyze the data obtained, a correlation relationship was proposed that establishes a connection between the specific heat capacity of solutions of porphyrin-NA-buffer complexes with the temperature dependence of the specific heat capacity of NA-buffer solutions and a contribution that takes into account changes associated with NA...porphyrin interactions that occur upon addition of porphyrin:

$$c_p(\text{NA-Por-Tris}) = a + b\times\Delta c_p(\text{NA-Por}) + c\times c_p(\text{NA-Tris}),$$
$$\text{where } \Delta c_p(\text{NA-Por}) = c_p(\text{NA-Por-Tris}) - c_p(\text{Tris}).$$

Previously, using a number of spectral methods, it was established that the studied porphyrins form two types of complexes with an external groove and intercalates with NA. Based on the results of the analysis of coefficients a, b and (1-c), it was found that these coefficients differ for two types of complexes. Porphyrin complexes with the external groove poly[d(AT)2] correspond to lower values of coefficients a and b and (1-c). The sequence of increasing parameters of the correlation relationships TMPy4P<PorN<PorS<TMPy3P<PorO coincides with the series of increasing affinity constants. The incorporation of porphyrin into the groove is accompanied by its complete or partial dehydration. It is obvious that porphyrins, when incorporated into the groove of poly[d(AT)2], destroy the highly ordered structure of water, and this occurs to the greatest extent in the case of Opor and to the least extent in the case of TMPy4P and PorN. The second group of porphyrin-poly[d(GC)2] complexes is characterized by large values of all three analyzed coefficients. This is due to the fact that significant structural changes occur in the solution due to the “NA-Por” interactions that occur when porphyrin is added.

The correlation parameters obtained for the porphyrin-poly[d(GC)2] systems are gross characteristics that reflect all changes in the solution that occur during the formation of two types of intercalation complexes.

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THERMODYNAMICS OF SUBLIMATION OF PERFLUORINATED SUBPHTHALOCYANINE

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Tetrapyrrolic macroheterocycles used in many fields as catalysts, semiconductors, nonlinear optical materials. Subphthalocyanines consist of three isoindole units containing boron as central atom.

The mass spectrometric study of the process of sublimation of F_{12}SubPc by the Knudsen method was carried out using the MI-1201 magnetic sector mass spectrometer modified for thermodynamic studies. The most intensive peak (m/z = 611 a.m.u.) in the electron impact mass-spectrum of F_{12}SubPc recorded at 541 K corresponds to a molecular ion without axial Cl ligand. The ions with m/z 411 ($(C_8F_4N_2)_2B^+$) and 211 a.m.u. ($C_8F_4N_2B^+$) can be attributed to 2/3 and 1/3 of F_{12}SubPc with borone.

Determination of the sublimation enthalpy for F_{12}SubPc included the measurement of the molecular ion intensity with a step-by-step decrease in temperature, and then with a step-by-step increase. The Figure 1 reflects the ln(IT) = f(1000/T) dependence for $F_{12}SubPc^+$ ion which can be proper approximated by straight line (R=0.9995). Each point of the graph corresponds to the ion current measured after its stabilization at a given temperature. The enthalpy of sublimation value ΔH_s calculated by linear regression using the Clausius–Clapeyron relation was found to be 189 (3) kJ*mol^{-1}.

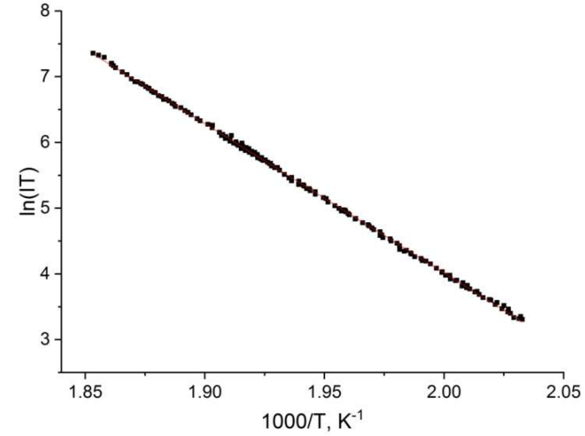

Figure 1. Temperature dependence of the molecular ion intensity logarithm in the range 492-539 K.

Results of our gas electron diffraction (GED) study of the F_{12}SubPcBCl molecule are in a good agreement to theoretical structural data (Table 1).

Table 1. Certain bond lengths (r_e, Å) in F_{12}SubPcBCl molecule. * - pcseg-2 basis set.

	GED	GED [1]	X-ray$_{ave}$ [2]	B3LYP*	B3LYP(D3BJ)*
r(Cl-B)	1.861(12)	1.917(34)	1.861(2)	1.862	1.855
r(B-N)	1.473(4)	1.459(10)	1.482(3)	1.490	1.487
r(N-C_α)	1.361(3)	1.366(9)	1.364(2)	1.364	1.365
r(C_γ-F)	1.327(3)	1.342(8)	1.338(2)	1.330	1.330

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UNSUBSTITUTED SUBPHTHALOCYANINE: THERMODYNAMICS OF SUBLIMATION

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Subphthalocyanines are lowest homologs of phthalocyanines, macrocyclic compounds which found a number of applications in organic electronic such as organic photoreceptors, photovoltaics, light-emitting diodes. The mass spectrometric study of the process of sublimation of unsubstituted subphthalocyanine (SubPc) by the Knudsen method was performed using the MI-1201 magnetic sector mass spectrometer modified for thermodynamic studies. The most intensive peaks in the electron impact mass-spectrum of SubPc correspond to a molecular ion $[M]^+$ (m/z = 430 a.m.u.) and its analogue without axial Cl ligand $[M\text{-}Cl]^+$ (m/z = 395 a.m.u.).

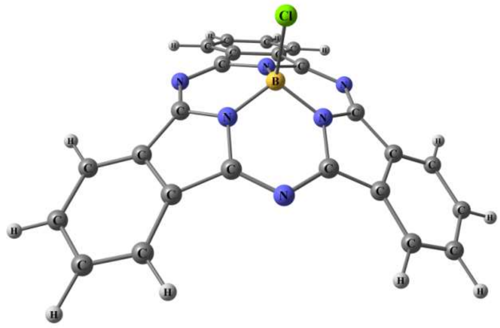

Figure 1. Molecular model of unsubstituted subphthalocyanine H_{12}SubPc.

Determination of the sublimation enthalpy of SubPc included the measurement of the molecular ion intensity with a step-by-step increase in temperature. The Figure 2 reflects the ln(IT) = f(1000/T) dependence for molecular ion $[M]^+$ and $[M\text{-}Cl]^+$ ion. Both of them can be proper approximated by straight line (R=0.999 and R = 0.997, respectively). Each point of the graph corresponds to the ion current measured after its stabilization at a given temperature. The enthalpy of sublimation value ΔH_s calculated by linear regression using the Clausius–Clapeyron relation was found to be 135 (5) kJ*mol^{-1}.

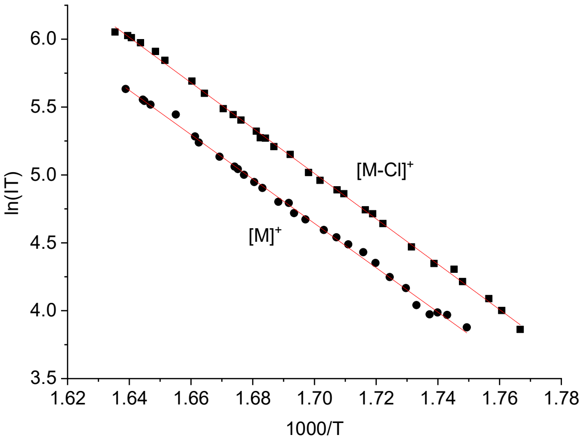

Figure 2. Temperature dependence of the molecular ion intensity logarithm in the range 565-613 K.

This work was supported by the Russian Science Foundation grant 20-13-00359.

SELECTIVE BINDING OF PH-CONTROLLED PORPHYRIN LANGMUIR-SCHAEFER FILMS

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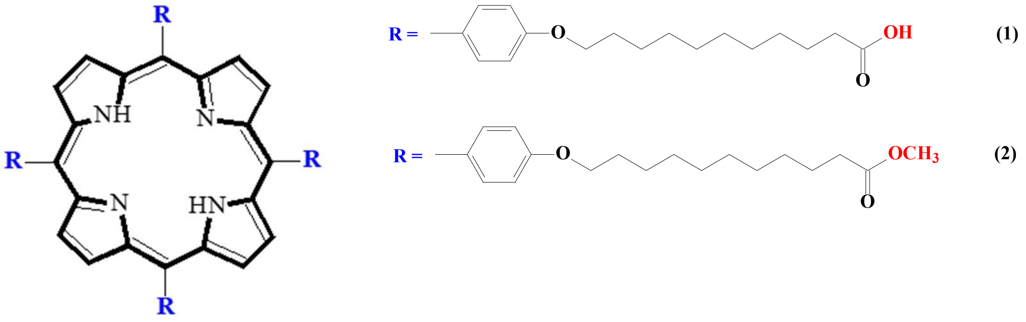
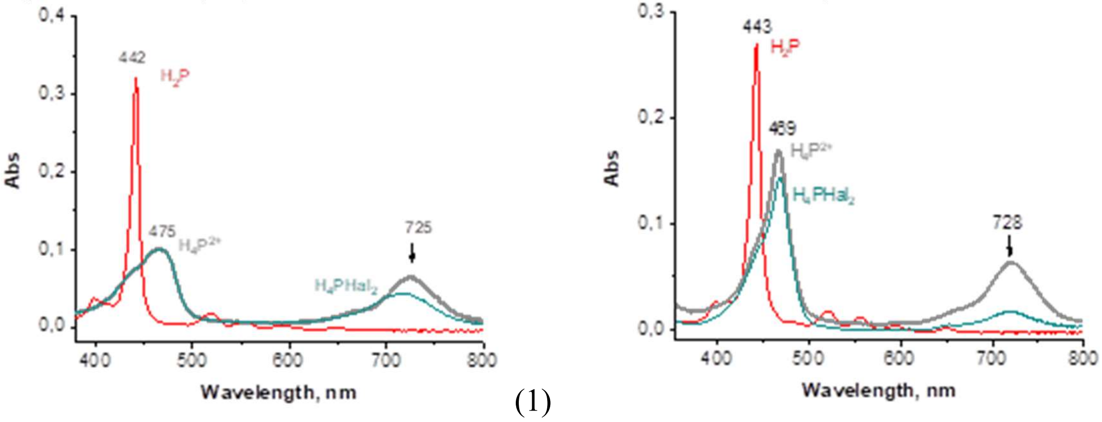
The floating layers formation conditions of 5,10,15,20-tetrakis(4-carboxydecyloxyphenyl)porphyrin (1) and 5,10,15,20-tetrakis(4-carboxymethyldecyloxyphenyl)porphyrin (2) at the air/water interface and Langmuir-Schaefer films (LS-films) obtained on glass and silicon substrates have been studied.



The floating layers were simulated and the geometric characteristics of molecular packings on water surface were calculated. Electron absorption spectroscopy showed that LS-films contain aggregates of J-type.

The basic properties of (1) and (2) in Langmuir-Schaeffer films have been investigated by the spectrophotometric titration method. It was found that the bis-protonated forms of porphyrins (1-2) (H_4P^{2+}) appear as halide-selective receptors. It forms stable $H_4P^{2+}(Solv)(X^-)$ in system $H_2P – (Bu)_4NX – HClO_4 – H_2O$ at 25°C ($X = Cl^-, Br^-, I^-$).



(1) (2)

Figure 1. UV-vis spectra of the LS-films (15 transfers) for the system $H_2P – (Bu)_4NI – HClO_4 – H_2O$ at 25°C.

The sensing and binding properties of the LS-films (with 15 transfers) with ammonia and formic acid in gaseous media have been studied. The results obtained can be used to design selective sensors for environmental pollution monitoring.

This work was carried out with the involvement of equipment of the Upper Volga Regional Centre for Physical and Chemical Research.

MIXED LIGAND COMPLEX FORMATION OF ZINC AND NICKEL(II) IONS WITH HISTIDINE, LYSINE AND ARGININE IN AQUEOUS SOLUTION

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A feature of arginine and lysine is the presence of not only α-amino and carboxylic groups, but also a highly basic ω-amino group and a guanidinium fragment, which often take part in the interaction with both metal cations and side substituents of other amino acids in mixed complexes. For this reason, ternary metal complexes with arginine and other amino acids and oligopeptides are being actively studied to identify interligand interactions, as this contributes to a better understanding of the behavior of metal ions in enzymes.

Previously, the study of ternary systems M(II) – His – L (M = Ni, Zn; L = Lys, Arg, Orn) was carried out mainly with a ratio of 1:1:1. Therefore, it was of interest to clarify the ionic composition of these solutions in a wide range of concentrations and to identify the features of coordination of ligands in mixed complexes based on a comparative analysis of stability constants and spectral data.

In this work, mixed ligand complexation of nickel (II) and zinc with natural L-histidine, L-arginine and L-lysine was studied. A series of pH-metric titrations of solutions ($M(NO_3)_2$ + HHis· HCl + HL· HCl) (M = Ni, Zn; L = Lys, Arg) with a solution of NaOH at 25 °C and ionic strength of 0.5 (KNO_3) at the ratios M : His : L = 1:1:1, 1:1:2 and 1:2:1 have been carried out. The processing of experimental data of pH-metric measurements was carried out according to RHMETR program [1].

An agreement between calculated and experimental curves at the ratio Ni : His : L = 1:1:1 was achieved by taking into account the formation of mixed complexes of the types MHisHL and MHHisHL (charges omitted) along with the MHisL complex (M = Ni; L= Lys). The formation of mixed complexes with three amino acid residues of the composition MH_nL_2His, MH_nLHis_2 (n=0, 1, 2, 3) (M = Ni, Zn) (charges omitted) was revealed. For the studied systems, the electron absorption spectra of solutions in the wavelength range of 350-980 nm were taken.

A correlation analysis of stability constants of the identified mixed complexes was also carried out. The symbate character in the change in stability constants of a number of mixed complexes of nickel and zinc with His on the one hand and Arg or Lys on the other hand indicates a similar, predominantly glycinate mode of coordination of lysine and arginine residues.

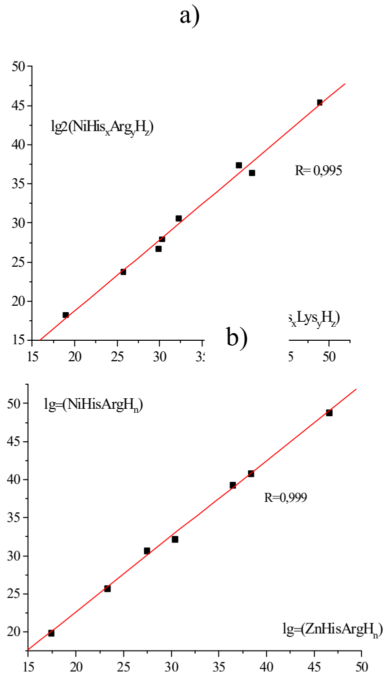

Fig. 1 Correlation dependences of the stability constants of mixed complexes of nickel (a) and zinc (b).

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SYNTHESIS, EXPERIMENTAL STUDY AND THERMODYNAMIC ASSESSMENT OF THE PYROCHLORE STRUCTURE HIGH-ENTROPY OXIDES

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The scientific problem that our work is aimed is the study of multicomponent ionic systems high entropy of mixing influence on the possibility of high-entropy crystalline solid solutions formation and stabilization in such systems. As part of solving this problem, in the course of our research we are studying the possibility of the formation of such solutions in complex oxide systems with pyrochlore structure (structure variant - $A_2B_2O_7$), and also studying the composition, crystal structure, properties of such systems and making its thermodynamic description, in order to obtain new compounds, which can become the basis for creating thermal barrier coatings with improved characteristics.

During the work, the method of solid-phase sintering is being used to synthesize high-entropy oxide phases with the pyrochlore structure. SEM, EDS and XRD are being used to confirm the composition and structure. The thermal expansion coefficients of the obtained materials are being studied, as well as their thermal conductivity and phase stability in a wide temperature range.

To date, there is practically no works aimed at a theoretical generalization of the experimental data obtained in this area. In particular, there are no works aimed at the thermodynamic description of the processes of formation and stabilization of high-entropy oxides with the pyrochlore structure.

For the thermodynamic description of the phases of this kind (and, in particular, for calculating the configurational entropy of mixing), it is traditional to use the sublattice model. As part of our work, we analyzed the applicability of such thermodynamic models of solid solutions as various variants of the sublattice model, combined with various approaches to describe deviations from ideality within one sublattice (polynomial model, Redlich-Kister model, Legendre polynomials), as well as various variants of the quasi-chemical model. Since high-entropy systems are multicomponent systems, the optimal interpolation approach for the systems under study was selected.

As part of the study, we carried out a thermodynamic description of the high-entropy crystalline phases with the pyrochlore structure. We based our analysis on literature and our own experimental data, primarily focusing on the temperature and concentration limits of stability of solid solutions in the studied systems. Expressions are obtained that relate the Gibbs energy of such phases to their composition and temperature. These results allow us to begin full-fledged thermodynamic modeling of phase formation processes in the systems under study. The result of such modeling will be both sections (poly- and isothermal) of the phase diagrams of the multicomponent studied systems, and the possibility of numerical simulation of the process of obtaining high-entropy crystalline phases with the pyrochlore structure.

The research was supported by the Russian Science Foundation grant No. 24-13-20009, https://rscf.ru/project/24-13-20009/ and with the support of the government of the Chelyabinsk region.

THERMODYNAMIC ANALYSIS OF HIGH-ENTROPY ALLOYS MELTS OXIDATION

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Possibilities of realization of high-temperature metallurgical processes involving metallic melts are determined by phase equilibria that occur between the components of a system consisting of metallic melt and non-metallic (primarily oxide) phases associated with it. Phase equilibria in such systems can be described by phase diagrams. T-x diagrams often allow, at best, at a qualitative level, to draw conclusions about how the compositions of the metal phase change when the qualitative composition of the phases with which they are in equilibrium changes. In such cases, it is more productive to use other methods of graphical representation of phase diagrams [1]. The information presented in the scientific literature about the interaction of the components of a metal melt with the formation of various metal-insoluble compounds, as a rule, refers to processes accompanied by the formation of individual substances. At the same time, it is well known that during real interaction processes of this kind, compounds of more than two elements are often formed, as well as various non-metallic phases of variable composition.

Especially diverse phase composition of interaction products involving alloying components of complex alloys. In addition, what elements the alloy consists of, the composition of the substances resulting from the interaction has a key influence on the concentrations of each of the elements that make up the alloy. Quantitative thermodynamic information on the influence of various factors on the composition of reaction products between the components of metal melts for wide ranges of variation of these factors is in many cases absent. Meanwhile, such information may be of great interest for improving a number of technological processes, including smelting, reagent refining, and alloying of complex alloys [1].

The objective of this part of the work was to study the possibility of calculating diagrams connecting the quantitative composition of a metal melt with the qualitative composition of conjugated non-metallic phases for high-entropy alloys, that is, alloys based on several metals in an equimolar or close to it ratio. In the studies carried out, the FactSage 8.0 software package was used (Phase Diagram module, diagram type – “liquidus projection”). Data from the SGTE2014 database (for modeling the metallic melt) and FToxid were used to model the oxide part of the systems under study. Also in the process of calculation the data of database for individual substances FactPS were used. In the course of the work carried out, diagrams of the type of interest to us were constructed and analyzed for the alloys $FeCoNiMnCr_x$, $FeCoNiCuAl_x$, $FeCoNiCrAl_x$, $FeCoNiCrCuAl_x$, $FeCoNiCrMnAl_x$, $FeCoNiCrSi_{0.5}Al_x$, $FeCoNiCrTiAl_x$.

The completed developments significantly expand the range of possibilities for thermodynamic research of systems “metallic melt / conjugated complex phases” by constructing phase diagrams from the point of view of increasing the number of objects of such studies, as well as from the point of view of increasing the clarity of presentation of the results of calculations.

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NON-MONOTONIC RELAXATION PROCESSES IN Ga-R (R = Nd, Sm, Gd, Tb, Ho) MELTS

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Gallium-based binary alloys are actively studied in recent years due to their properties and considered as promising materials in various industries: semiconductor materials in high-temperature rectifiers and transistors, solar cells and other devices. Liquid gallium alloys are used in the manufacture of high-temperature thermometers and manometers and as coolants in nuclear reactors [1]. However, to date, the structure-sensitive properties of gallium-based alloys are not widely investigated. Density and viscosity of gallium - rare earth metal (R) alloys in a wide temperature range have been experimentally investigated in present work for the first time.

Ga-R (R = Nd, Sm, Gd, Tb, Ho) alloys containing up to 5 at. % of rare earth metals were obtained in a resistance furnace from pure components (Ga 99.95%, R 98.5%). The composition of the samples was checked using Spectrum Flame Modula S atomic absorption spectrometer. Density of the alloys was studied by gamma-absorption method on an automated set-up in temperature range 293 - 1500 K. The relative error of measurements was less than 1%. Viscosity of the melts was investigated by automated units implementing method of damped torsional vibrations of the crucible with melt (Shvidkovsky method) in temperature range from liquidus temperature to 1500 K in crucible configuration with a lid and without it. The relative error of measurements was less than 3%. Additionally, isotherms of density and viscosity of the melts were obtained.

It was found that at the melting point of gallium, the alloys transition to a two-phase state. Transition from two-phase state to liquid state at heating is strongly extended in temperature for all investigated compositions. Mismatch of density and viscosity polytherms of melts during heating and subsequent cooling (hysteresis) was found in liquid state. Non-monotonic long-term changes in density and viscosity (relaxation processes) were detected for the first time based on the results of properties measurements which can be related to their transition to a more homogeneous state. Relaxation of properties were found to extend up to 5-6 hours depending on the type of R used. Values of density and viscosity of the melts after relaxation coincide with the values obtained after their heating to 1500 K by measuring the temperature dependences.

Obtained results can be used for numerical modelling of properties of Ga-R binary melts characterized by relaxation processes, as well as for their further practical use in industry.

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THEORY OF ELECTROLYTE SOLUTIONS IN A SLIT CHARGED PORE TAKING INTO ACCOUNT THE STRUCTURAL INTERATIONS OF IONS AND SPECIFIC ION ADSORPTION

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Modelling electrolyte solutions within charged slit nanopores is an important concern for a variety of scientific and technological applications, such as constructions of supercapacitors and batteries, systems for water purification, ion transport in cell membranes through ion channels. These systems implicate unresolved tasks, among which are the accurate modeling of structural interactions of ions in confined geometries, the effects of specific ion interactions and electrostatic interactions [1,2].

Self-consistent field theory is a powerful but limited method for modelling the behavior of liquid-phase ionic systems. To overcome method's limitations we proposed a method based on Blossey et al.[3] with addition of structural interactions through a bilinear form over the gradients of local ionic concentrations in the grand thermodynamic potential and their steric interactions through the lattice gas model. We investigated the behavior of ion concentration profiles and disjoining pressure as function of the ionic concentrations at the middle of pore.

The formulated model of spatially inhomogeneous electrolyte solutions allows to demonstrate a number of phenomena. Firstly, the disjoining pressure was calculated through proposed approach [4]. Secondly, taking into account the structural interactions leads to the region of negative values of the disjoining pressure on its dependences on the pore thickness and to a noticeable global minimum at sufficiently small pore widths, while on large scales, the exponential drop of the disjoining pressure known from the The Derjaguin-Landau-Verwey-Overbeek theory is recorded [5]. Finaly, the inclusion of ion attraction to the pore walls strengthens and shifts the region of 'structural' wall attraction towards smaller pore thicknesses.

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CHEMICAL THERMODYNAMICS ON POST STAMS

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World philately reflects numerous images of scientists who have made a significant contribution to the development of chemical thermodynamics (Figure 1).

Figure 1. Post stamps: a – A. Celsius; b – M. Berthelot; c – H. von Helmholtz; d – F. Haber; e – J.H. van't-Hoff; f – J.W. Gibbs; g – L. Boltzmann; h – J.D. van der Waals; i,j – W.H. Nernst; k – M. Planck, l – K. Caratheodory

PHONON DENSITY OF STATES AND THERMODYNAMIC FUNCTIONS AT HIGH TEMPERATURES OF CADMIUM TUNGSTATE

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Cadmium tungstate has been an interesting object for researchers for many years due to its unique properties, which determine a number of practical applications. For example, it is used as a Raman laser material [1,2], as a detector in spectrometric and radiometric devices, including X-ray computed tomography [3]. Also, $CdWO_4$ is a promising bolometric detector material for rare event searches, including the search for neutrinoless double beta decay [4,5]. Currently, many properties of cadmium tungstate have been widely investigated, but information on its density of states is absent. There are also no data on its heat capacity and thermodynamic functions in the high temperature range.

In this study, we used a numerical method of solving the inverse problem [6,7]. This method enabled us to obtain, on the basis of high-precision data on low-temperature heat capacity, the phonon density of states with a shape description includes three or four peaks with a correct distribution of the number of vibrational modes over frequencies. The phonon density of states of $CdWO_4$ was calculated from the low-temperature heat capacity obtained by both relaxation and adiabatic calorimetry methods in reference [8]. The calculation was carried out in the following sequence. First, a series of test calculations was made with a large frequency step of 64 K. This allowed us to estimate the boundary frequency and the spectrum shape, as well as to determine the temperature range where the initial experimental heat capacity does not have a significant anharmonic contribution. Next, several zero approximations were selected, and a series of calculations was performed for each of them with a frequency step of 16 K. Finally, the obtained solutions were averaged, and the uncertainty was evaluated. As a result, the phonon density of states of cadmium tungstate was obtained.

The characteristic temperatures associated with the main moments of the phonon density of states have been calculated. It is important to note that the first moment of the density of states is calculated with high accuracy, which is due to the correct accounting of the number of vibrational modes at different frequency intervals. The knowledge of the first moment allowed us [7] to calculate the zero-point energy of crystal lattice vibrations of cadmium tungstate. Additionally, the characteristic Debye temperature at $T \to \infty$ was also determined.

Using the phonon density of states, isochoric heat capacity of $CdWO_4$ was calculated in the entire region of solid phase existence. Subsequently, the thermodynamic functions of entropy, internal energy and Helmholtz free energy were calculated.

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PHONON DENSITY OF STATES AND THERMODYNAMIC FUNCTIONS AT HIGH TEMPERATURES OF ZINC TUNGSTATE

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Zinc tungstate shows promise as a cryogenic bolometer, laser material, and scintillator [1–3]. While $ZnWO_4$ has been extensively researched and many of its properties have been studied, such as its crystal structure temperature dependence [4], melting point (1473 K) [5], experimental heat capacity at constant pressure [6–8], and enthalpy increment [9], there is a lack of information in the literature regarding its phonon density of states, main characteristic temperatures, and isochoric heat capacity and thermodynamic functions.

The numerical method [10,11] to solve the inverse problem was used in this study. This method allowed us to obtain the phonon density of states (pdos) based on high-precision data on low-temperature heat capacity. The pdos shape description includes three or four peaks with a correct distribution of the number of vibrational modes over frequencies. The phonon density of states of $ZnWO_4$ was calculated from the experimental low-temperature heat capacity data [7,8]. The calculation was performed in the following sequence. First, we conducted a series of test calculations using a large frequency step of 64 K. This enabled us to estimate the boundary frequency and spectrum shape, as well as determine the temperature range where the initial experimental heat capacity does not have a significant anharmonic contribution. Next, several zero approximations were selected, and a series of calculations was performed for each of them with a frequency step of 16 K. The obtained solutions were then averaged, and the uncertainty was evaluated. This resulted in the determination of the phonon density of states of zinc tungstate. The uncertainty estimation of the obtained solution is also made.

The main moments of the phonon density of states and the characteristic temperatures associated with them have been calculated. The first moment's knowledge enabled us [11] to calculate the zero-point energy of crystal lattice vibrations of zinc tungstate with high accuracy.The characteristic Debye temperature at $T \to \infty$ was also determined.

The isochoric heat capacity of $ZnWO_4$ was calculated throughout the solid phase using the phonon density of states. Afterwards, the thermodynamic functions of entropy, internal energy, and Helmholtz free energy were also calculated.

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CRYSTALLISATION OF COCRYSTALS BY SUBLIMATION: A CASE STUDY OF 4-AMINOBENZOIC ACID

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Cocrystal formation established itself as a useful technique to fine-tune physical properties of substances. Despite the use of a variety of approaches to cocrystal synthesis, most of them are solution-based approaches and require utilization of organic solvents. It is well known that sublimation is an underused crystallization method that is solvent-free, i.e. ‘green’, and can allow to produce cocrystal materials in high purity. The recent studies show the perspective and advantages of cocrystallization by sublimation [1]. This approach can be seen not only as an alternative method of producing multicomponent solids, but also as a unique way of obtaining new crystalline forms, including polymorphs, stoichiomorphs and so on [2]. At the same time the fundamentals of the cocrystal sublimation process are still poorly understood.

The present work is an in-depth investigation of the sublimation processes of 4-aminobenzoic acid binary cocrystals. 4-aminobenzoic acid was chosen as a prospective model compound because it is stable over a large temperature range and forms a variety of multicomponent solid forms. Based on Cambridge structural database analysis a series of cocrystals was chosen for further investigation. Sublimation experiment has been conducted using Schlenk tube fitted with a coldfinger condenser. As an initial phase we were used pure cocrystals, physical mixtures of parent compounds and substances in special separate vials. According to the results of these experiments, the influence of the properties of initial compounds on the purity of the cocrystals was analyzed. It was concluded that pure cocrystal formation is observed only when the sublimation enthalpies and Gibbs energy values of cocrystal components are close to each other. For cocrystals with close sublimation parameters of parent compounds, vapour pressures of cocrystal components were measured.

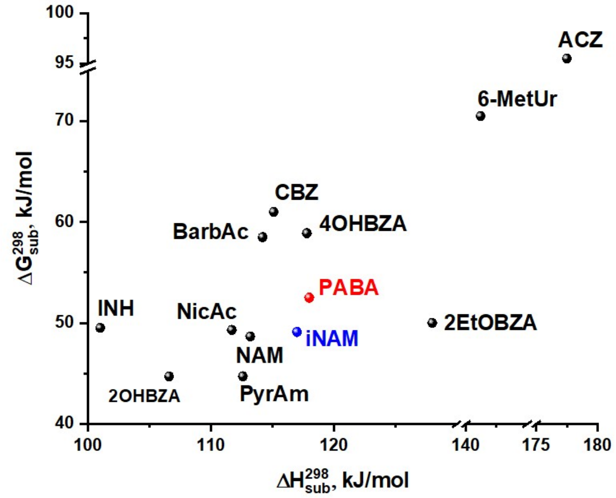

Figure 1. Sublimation parameters of compounds used for cocrystal sublimation experiment

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THE THERMODYNAMIC MODELING OF THE FORMATION OF HIGH-ENTROPY PHASES

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The traditional approach to develop materials based on single principal component has largely exhausted its potential, particularly in terms of further improving the multifunctional properties of catalysts. The concept of materials with multiple principal components stabilized by high entropy of mixing offers a promising path to overcome the limitations of traditional approaches, as it provides sufficient range to vary the chemical composition and structure of materials.

The goal of our research is to develop (based on modeling results using CALPHAD - CALculation of PHAse Diagrams) high-entropy materials with an ordered crystal structure for highly efficient electrocatalytic reduction of carbon dioxide.

As part of this area, research is being conducted aimed at developing and optimizing the composition and morphology of a number of catalysts based on high-entropy materials of two types (high-entropy intermetallic compounds and high-entropy oxides) for the electrocatalytic reduction of CO2 to produce C1 and C2 products. The possibilities of creating such highly efficient and inexpensive catalysts based on high-entropy intermetallides and transition metal oxides (mainly), as well as composite materials based on them in the form of micro- and nanoparticles, as well as in the form of porous materials, are being studied.

Thermodynamic modeling using CALPHAD algorithms is used for initial screening and optimization of the chemical composition of high-entropy catalytic systems, as well as for the search for single-phase high-entropy intermetallic compounds or oxides. Using the thermodynamic modeling tools available to the team (FactSage and Thermo-Calc along with the necessary databases), a search for thermodynamically stable compositions related to the systems under study is carried out.

Methods for the rational selection of values of thermodynamic functions have been developed, which are planned to be used to analyze the results obtained during the implementation of the project and the physical and chemical description of the studied systems.

The results of the work are thermodynamic modeling of the formation of the studied high-entropy phases and the results of predicting new single-phase high-entropy intermetallic compounds and high-entropy oxides using programs that implement CALPHAD algorithms.

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THE THERMODYNAMIC MODELING OF STRENGTHENING CARBIDES FORMATION FROM HIGH-ENTROPY ALLOYS COMPONENTS

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The study of the formation and stabilization processes, as well as the physicochemical characteristics of composite materials based on multi-principal element alloys (high-entropy alloys), the development of new systems of this kind and the study of the systems samples properties to establish the possibility of their use as structural materials and coatings is one of the urgent tasks of modern materials science.

This work is devoted to the development of new surfacing materials based on the Al-Co-Ni-Fe-Cr-W-C, Mn-Co-Ni-Fe-Cr-W-C, Co-Ni-Fe-Cr-W-C systems. It is planned to create composite materials that combine a high-entropy matrix with endogenous reinforcing carbide particles. In order to optimize the compositions of the materials being developed, determine the temperatures of possible phase transformations, and the conditions for the release of endogenous strengthening particles, thermodynamic modeling of phase equilibria in the systems under study is used.

In the process of performing work, modern methods for performing calculations of this kind are used, implemented in modern specialized software (FactSage 8.0 and Thermo-Calc 2023b). During the modeling process using FactSage, the SGTE and SGPS databases were used (at the first stage of the work, model parameters of other databases were used, but analysis of experimental data led to the conclusion that it was necessary to replace the set of model parameters). In the process of using Thermo-Calc for modeling, a specialized thermodynamic data base for describing high-entropy alloys (TCHEA5) was used.

During thermodynamic modeling, we used both traditional methods of equilibrium thermodynamics, on which the CALPHAD approach is based, and a model of nonequilibrium crystallization of melts (various versions of the Sheil model), which allows a more correct description of the process of real crystallization of metals than using the equilibrium crystallization model.

The information obtained during modeling allows us to draw conclusions both about the processes occurring during the smelting and crystallization of metal, and about the processes that can occur during long-term operation of composite materials at elevated temperatures.

The calculation results demonstrate how changes in the composition of the systems under consideration and changes in temperature lead to changes in the composition of the equilibrium phase compositions. The diagrams constructed during the work show the boundaries of the phase equilibrium regions and, in particular, the concentration boundaries within which we can count on the thermodynamically stable coexistence of a high-entropy phase (with a BCC or FCC structure) with the reinforcing carbides phase.

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STUDY OF THE HEAS/CARBIDES COMPOSITES PHASE STRUCTURE STABILITY

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As part of the work aimed at creating new composite surfacing materials based on the Al-Co-Ni-Fe-Cr-W-C, Mn-Co-Ni-Fe-Cr-W-C, Co-Ni-Fe-Cr-W-C systems, which include matrix from high-entropy alloys (HEAs) with endogenous reinforcing carbide particles, the experimental samples were studied.

To prepare experimental samples from metal melts, weighed mixtures of simple substances were used. To obtain alloys, powders and pieces of simple substances with a purity of at least 99.99% were used.

The alloys were smelted in corundum crucibles in a vacuum laboratory furnace with graphite heaters. The temperature in the furnace was brought to 1650 °C at a rate of 600 °C/hour, then held for at least 30 minutes to average the composition of the samples, after which the furnace was cooled at a rate of 600 °C/hour and the crucibles were removed from the working space.

After that, the obtained ingots were removed from the crucibles (the crucibles were broken) and cut. The obtained metal (most of it) was subjected to heat treatment/homogenization in the same furnace at temperatures of 400, 600, 800, 1000 °C for 5 hours.

Then the obtained samples were studied by scanning electron microscopy, EDS and XRD (which made it possible to confirm their composition, as well as find out their structure), as well as were studied of the stability of the phase composition and heat resistance.

An experimental study of the stability of the samples under study by thermal analysis was carried out primarily through differential scanning calorimetry, implemented using a NETZSCH STA 449 F3 Jupiter simultaneous thermal analysis device. The study was carried out in the temperature range of 20-1100 °C, both in an argon atmosphere and in an atmosphere containing oxygen and nitrogen (in addition to phase transformations, such an atmosphere makes it possible to estimate the increase in the mass of samples as a result of possible oxidation of the metal). Heating and cooling rates is 5 °C/min. Judging by the data obtained, the studied systems are quite resistant to oxidation in the temperature range under consideration.

For most of the studied compositions, phase transformations are not detected by the method used. However, in one of the samples belonging to the Al-Co-Ni-Fe-Cr-W-C system, a noticeable transformation occurs at temperatures of about 600 °C, which is probably the BCC ↔ FCC transformation.

An experimental study of the heat resistance of the obtained samples by thermal analysis was carried out using the derivatography method, implemented using a thermal analysis device (derivatograph) Q-1500 D. The heating rate in an air atmosphere was set to 5 °C/min. The studied temperature range is 20-1300 °C. The results of the experimental study demonstrate the high resistance of the studied systems to oxidation at temperatures below 900–1000 °C. This indicates the promise of using the developed materials in high-temperature applications.

The results of thermal analysis were compared with the results of thermodynamic modeling of the studied systems.

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THE THERMODYNAMICAL PROPERTIES OF ALKYL-SUBSTITUTED 1,3-DIOXOLANES MODELING BY ADDITIVE METHODS

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The traditional additive method of group contributions, despite the simple and understandable classification of structural fragments, does not adequately describe the thermodynamic properties of cyclic acetals, which include alkyl-substituted 1,3-dioxolanes. In the group contribution method, in addition to taking into account the short-range 1,2- and 1,3-intramolecular interactions, only partial accounting of the longer-range 1,4-interactions is provided using the *gauche*-correction for substituent interactions.

We have developed a semi-empirical method for determining the values of thermodynamic properties 2-, 4-, 2,2-, 2,4-, 2,2,4- alkyl-substituted series of 1,3-dioxolan at 298.15 K. The technique is based on the additive determination of the numerical values of the increments of replacement of hydrogen atoms in the cycle and substituents by the corresponding alkyl groups and full consideration of 1,4-intramolecular interactions of various types. The classification of intramolecular interactions involves distinguishing 1,4-interactions of substituents with the nearest atoms of the cycle (1,4-(C,C) and 1,4-(C,O), 1,4-interactions in substituents, as well as *cis*-interactions of substituents in the cycle. The value of the property of 1,3-dioxolan at a temperature of 298.15 K was assumed to be known, and the remaining fractions of the property and interactions were summed up with it.

According to the totality of experimental values of the thermodynamic properties of alkyl-1,3-dioxolanes (298.15 K): $\Delta_f H_m^0$ (l.,g.) (10 compounds), $\Delta_l^g H_m^0$ (11 compounds), $C_{p,m}^0$ (l.) (10 compounds)) [1-3] numerical values of 9 replacement increments and interactions were found, which can be used to model the values at 298.15 K of these properties of compounds of the considered series, which have not been studied experimentally. The relative errors in reproducing the values of properties by calculation are at the level of experimental errors in obtaining initial data: 0.14 % for $\Delta_f H_m^0$ (l.), 0.99 % for $\Delta_l^g H_m^0$, 0.05 % for $\Delta_f H_m^0$ (g.) and 1.5 % for $C_{p,m}^0$ (l.). The values of $C_{p,m}^0$ (l., 298.15 K) of 4-methyl-1,3-dioxolan (154.1 ± 0.6) $J \cdot mol^{-1} \cdot K^{-1}$ [2] and 2,2,4-trimethyl-1,3-dioxolan (213.8 ± 0.9) $J \cdot mol^{-1} \cdot K^{-1}$ [3] obtained by the low-temperature adiabatic calorimetry are well reproduced by calculation, their relative errors do not exceed 0.1 %.

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ISOTHERMAL TITRATION CALORIMETER FOR STUDYING THE PROCESSES OF DISSOLUTION, MIXING AND COMPLEXATION IN SOLUTIONS

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Isothermal titration calorimeters are used in scientific practice to study a wide range of interactions in solutions, ranging from interactions of simple small molecules to association in surfactant solutions and complexation in solutions of proteins and other polymers.

A titration calorimeter has been created based on a steel block of the MS 80 D calorimeter (Setaram) holding a battery of 1316 thermocouples, two platinum thermometers and a heater. The thermostat control is carried out by a proportional-integral-derivative controller (BIC, Belarus). Temperature fluctuations in the control zone do not exceed 0.002 degrees. To measure thermal effects, two reaction cells (in the figure) and a thermopower and electrical resistance meter (BIC, Belarus) were designed and manufactured. The calorimeter as well as measuring and control devises was additionally placed into an air thermostat with the temperature of 293 ± 2 K.

The reaction volume of the cells is approximately 30 ml. The cells are equipped with mixers, the shafts of which are driven by stepper electric motors. It is shown that the baseline fluctuations are ±16 nV, which corresponds to a heat flux power of ±1.5 μW.

The report describes in detail the design of the calorimeter and reports the results of its chemical calibration using standard substances: 10 wt. % n-propanol solution, sucrose solutions and urea solutions at 298.15 K. The performance of the calorimeter for the joint determination of enthalpies and interaction constants is demonstrated using the example of the reaction between 18-crown-6 ether and barium nitrate.

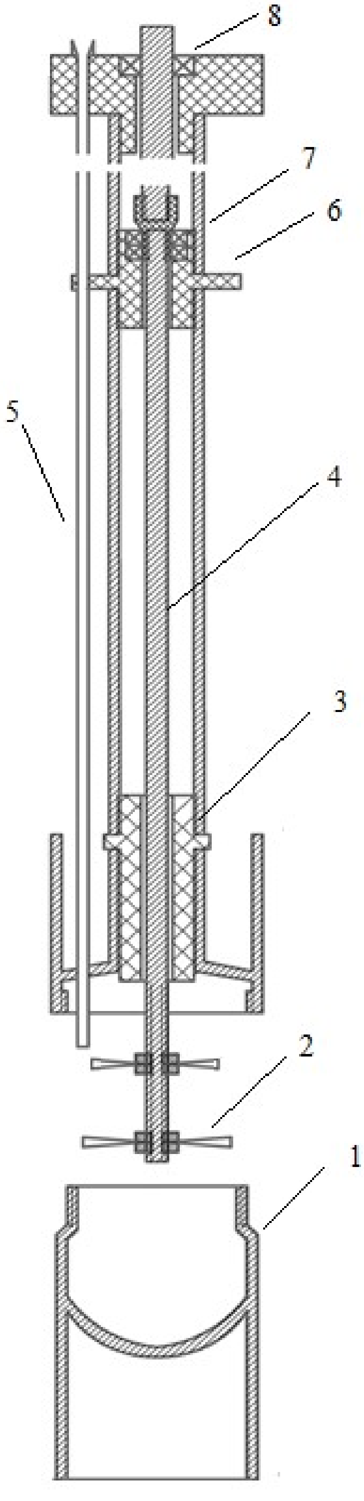

Figure. The calorimetric cell: 1 - a stainless steel calorimetric vessel with the volume of 25 ml, 2- a stainless steel stirrer, 3, 6 – thermal connector polyacetal couplings, 4 – a stirrer rod, 5 – a tube for injecting a solution with a gas-tight Hamilton syringe-capillary system, 7, 8 – low noise bearings

HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF CRYSTALLINE URIDINE FROM 0 TO 320 K

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Uridine is a representative of nucleosides. Nucleosides and their derivatives are successfully used in the creation of drugs against various types of cancer and viral infections. Therefore, these substances are currently very popular objects for research. Modern drug discovery methods involve screening large numbers of compounds, both individually and in mixtures. The use of thermodynamic measurements plays an important role in both high-throughput identification of binders and fundamental understanding of molecular interactions, which is central to rational drug design. It is also important to have reliable thermodynamic data to determine the likelihood of a chemical reaction or the stability of a compound in a complex biological system.

In this work, we present the results of experimental studies of the thermodynamic properties of uridine at low temperatures. These studies were performed for the first time for uridine.

The uridine ($C_9H_{12}N_2O_6$; CAS Number: 58-96-8) sample was prepared and purified by Sigma-Aldrich. Prior to heat capacity measurements, additional control tests of the sample were conducted in order to identify and confirm the claimed purity using infrared absorption spectroscopy, X-ray phase analysis, and elemental analysis.

IR spectra of the sample were recorded at room temperature on a Scimitar FTS-2000 IR Fourier spectrometer, in KBr pellets, in a wavenumber range 400 – 4000 cm^{-1}. The data obtained are in good agreement with the literature. No other absorption bands were found. The X-ray phase analysis of the polycrystalline sample was performed at room temperature with a Shimadzu XRD-7000 X-ray diffractometer. The experimental diffractogram fully matches the theoretical for monocrystalline uridine. The elemental analysis for determining C, H, and N was performed with a vario MICRO cube CHNS analyser (Elementar Analysensysteme GmbH, Germany). Chemical analysis of the purified compound showed that the composition of C, H and N corresponds to the calculated one within the accuracy of the analysis. For the determination of impurities in the sample a microwave plasma atomic emission spectrometer 4100 MP-AES (Agilent Technologies, USA) was used. The impurity content in the sample does not exceed 0.2%.

The heat capacity of the sample was measured in the range from 5 K to 320 K in the vacuum adiabatic calorimeter (laboratory-made) described earlier [1]. Liquid helium, liquid nitrogen, and ice were used in the cryostat to cool the calorimeter. No thermal anomalies were detected in the functional behaviour of heat capacity; therefore, uridine does not undergo any phase transformations in the temperature range under examination. The experimental values of heat capacity were used to compute integral thermodynamic functions (entropy, enthalpy, and reduced Gibbs energy) in the range of 0 to 320 K. The standard entropy of crystalline uridine formation was determined at T=298.15 K.

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LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF $LiCsMo_3O_{10}$

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The most important problem of nuclear and particle physics is the search for the neutrinoless double beta decay (0v2β decay) of atomic nuclei. The technique of cryogenic scintillation bolometers is being developed to search for 0v2β decay. In this regard, there is an active search for new scintillation materials. In particular, in new generation experiments on search and registration of neutrinoless double beta decay crystalline scintillators are required, containing certain elements, for which this type of decay is theoretically possible. The most promising scintillators in this regard are single crystal double alkali metal molybdates. This work presents data on the thermodynamic properties of $LiCsMo_3O_{10}$ in the range of 0 – 300 K. The presented results were obtained for the first time.

The single-crystal of $LiCsMo_3O_{10}$ was grown using the low-gradient Czochralski method [1]. Samples of various sizes were made from the resulting single crystal for further research. Information on the composition and content of impurities was obtained by X-ray photoelectron spectroscopy (FlexPS, SPECS) and atomic emission spectroscopy (ThermoScientific ICAP-6500). Data on crystal lattice parameters were obtained over a wide temperature range (Bruker DUO diffractometer). Quantitative elemental analysis showed an impurity content of less than 0.1% in the sample.

The heat capacity of the sample $LiCsMo_3O_{10}$ was measured using the adiabatic calorimetry method in the range of 5 – 300 K. More detailed information about the calorimeter is presented in earlier work [2]. The sample was placed in a calorimetric ampoule made of nickel with a volume of 12 cm^3. The temperature of the calorimeter was measured with a standard platinum resistance thermometer. No anomalies associated with phase transitions were detected in the behavior of the heat capacity. Thermodynamic functions were calculated based on heat capacity in the range of 0 – 300 K. For absence of experimental data for temperatures below 5 K, the thermodynamic function calculations assumed that the sample's heat capacity had no anomalous contributions in this area and followed the Debye limiting law. The characteristic Debye temperature $\Theta_D(0)$ was calculated. When calculating the Debye temperature $\Theta_D(0)$, we used the approach described in detail in the article [3].

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HEAT CAPACITY OF PIVALOYLTRIFLUORACETONATE YTTRIUM $Y(C_8H_{10}F_3O_2)_3$

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Yttrium pivaloyltrifluoroacetonate (or $Y(C_8H_{10}F_3O_2)_3$) belongs to the class of metal beta-diketonates that crystallize in a molecular type lattice. Yttrium beta-diketonates are used as precursors in the production of superconducting materials, heat-resistant coatings, etc. by chemical vapor deposition. This paper presents the results of the experimental determination of the heat capacity of $Y(C_8H_{10}F_3O_2)_3$ by the method of adiabatic calorimetry. These results were obtained for the first time.

A commercial sample of yttrium pivaloyltrifluoroacetonate was purified as described in [1]. The sample was characterized in detail by X-ray phase analysis (Shimadzu XRD-700), IR spectroscopy (Scimitar FTS2000) and chemical analysis for the composition of C, H and F (Carlo-Erba 1106). The thermal stability of the complex was studied over a wide temperature range (from 300 K to the melting point) using a NETZSCH TG 209 F1 Iris thermogravimetric analyzer. The IR spectra and derivatograms of the sample correspond to the class of compounds under study [1]. The experimental diffraction pattern completely coincides with the theoretical one, calculated from the data of [1] for a single crystal. Chemical analysis of the purified compound showed that the composition of C, H and F corresponds to the calculated one within the accuracy of the analysis. The mass fraction of the main substance in the sample was at least 99%.

The heat capacity of the sample was measured in the range from 5 to 310 K using a vacuum adiabatic calorimeter (laboratory made), described previously [2].

In experimental data on heat capacity, an increased scatter of points is observed in the region of 20 – 30 and 210 – 240 K; no other anomalies in the functional behavior of the heat capacity associated with phase transitions were detected in the entire temperature range under consideration. Based on the data obtained, smoothed values of heat capacity, entropy, enthalpy and reduced Gibbs energy were calculated in the temperature range from 0 K to 300 K.

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TOPICAL BIOCOMPATIBLE HYDROGELS OF iota-CARRAGEENAN CONTAINING SOME CHEMOTERAPY AGENTS

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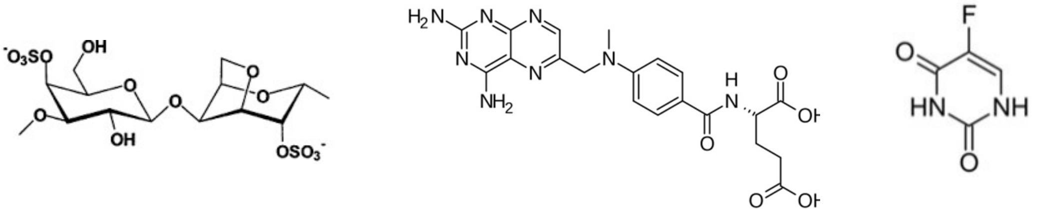
In the field of oncology, methotrexate (MTX) and 5-fluorouracil (5-FU) are well-known antimetabolite drugs employed for treatment of various types of cancer. However, their oral administration often results in significant toxic side effects, prompting researchers to explore alternative delivery methods. One promising approach is the development of topical gel formulations.

This research is focused on development of hydrogel composites consisting of natural and biocompatible iota-carrageenan (iCR) and MTX or 5-FU. The rheological properties of iCR/MTX and iCR/5-FU composite gels were examined. It was observed that the structural organization of iCR gels is enhanced in the presence of 5-FU and MTX. This effect is caused by possible interactions between drug molecules and polymeric chains. Drug-iCR interactions were characterized by means of ^{1}H NMR and FTIR spectroscopy. Based on the obtained data it was shown that MTX, possessing numerous polar functional groups, exhibits the strongest affinity to iCR in comparison with 5-FU.

The release of 5-FU and MTX from hydrogels was investigated. It was found that 5-FU release from the gel occurred more rapidly and to a larger extent compared with MTX. The mechanisms of 5-FU and MTX release from iCR hydrogels were determined and the impact of drug structure on these processes was evaluated.



iCR MTX 5-FU

Structural formulas of objects under study

LOW TEMPERATURE THERMODYNAMIC PROPERTIES OF γ-KGd(MoO_4)$_2$

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Double molybdate of potassium with gadolinium (KGd(MoO_4)$_2$) has high magnetocaloric effect characteristics [1], which makes it a promising material for magnetic refrigeration technology, characterized by high cooling efficiency and lower energy consumption compared to traditional methods [2]. To better understand the dependence of cryogenic magnetocaloric characteristics on the structure of the substance and the parameters of phase transitions, it is of particular interest to measure the heat capacity in the low-temperature region and study the thermodynamic properties of such materials.

In this work, a study was carried out of the low-temperature thermodynamic properties of the γ-modification of KGd(MoO_4)$_2$. All results were obtained for the first time.

The sample was manufactured at the Nikolaev Institute of Inorganic Chemistry SB RAS and was a collection of single-crystal plates. Before conducting the research, the sample was characterized by X-ray phase analysis (Shimadzu XRD-7000 diffractometer), X-ray fluorescence analysis (Bruker M1 Mistral spectrometer) and inductively coupled plasma atomic emission spectrometry (VMK-Optoelectronics Grand-ISP spectrometer). The resulting X-ray pattern corresponds to the orthorhombic γ-modification of KGd(MoO_4)$_2$. Based on the results of X-ray fluorescence analysis and atomic emission spectrometry, it can be judged that the purity of the sample is at least 99%.

The heat capacity of the sample was measured using a vacuum adiabatic calorimeter (laboratory made). The cryostat of the calorimeter was described in detail previously [3]. A new calorimetric ampoule with a volume of 2 cm^3, made of nickel, was used for measurements. Temperature was measured with a platinum resistance thermometer. The reliability of the calorimetric device was confirmed by measurements of the heat capacity of benzoic acid.

Data on the heat capacity of γ-KGd(MoO_4)$_2$ were obtained in the range of 5 – 300 K. No thermal anomalies were identified in the functional behavior of the heat capacity. Based on the data obtained, integral thermodynamic functions (entropy, enthalpy increment, reduced Gibbs energy) were calculated in the range 0 – 300 K. As a result of the calculations, the phonon component of the heat capacity was determined, and data on the Debye temperature and moments of the density of phonon states were obtained.

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The study was supported by a grant from the Russian Science Foundation No. 24-19-00405, https://rscf.ru/project/24-19-00405/

DISTRIBUTION AND PERMEABILITY OF PYRIDINECARBOXAMIDE DERIVATIVES FROM BUFFER AND CYCLODEXTRIN SOLUTIONS

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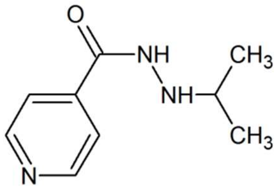
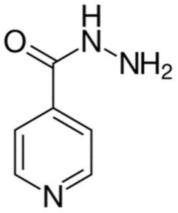
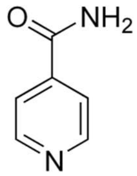
The main aims of the study were to disclose the influence of the structure on the solubility, distribution and permeability of the parent substances, iproniazid (IPN), isoniazid (INZ) and isonicotinamide (iNCT), at 310.2 K and to evaluate how the presence of cyclodextrins (2-hydroxypropyl-β-cyclodextrin (HP-β-CD) and methylated β-cyclodextrin (M-β-CD)) affects the distribution behavior and permeability properties of a model pyridinecarboxamide derivative, iproniazid (IPN).



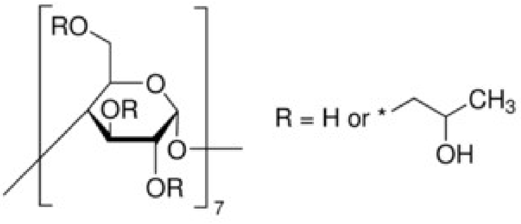
IPN



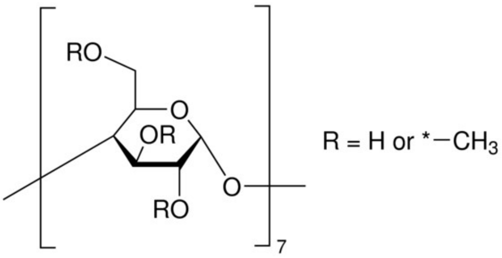
INZ



iNCT



HP-β-CD



M-β-CD

The following order of decreasing the distribution and permeability coefficients was estimated: IPN > INZ > iNAM. A slight reduction of the distribution coefficients in the 1-octanol/buffer pH 7.4 and n-hexane/buffer pH 7.4 systems (more pronounced in the first system) was revealed. The extremely weak IPN/cyclodextrins complexes were estimated from the distribution experiments: K_C(IPN/HP-β-CD) > K_C(IPN/M-β-CD). The permeability coefficients of IPN through the lipophilic membrane - the PermeaPad barrier - were also measured with and without cyclodextrins in buffer solution. Permeability of iproniazid was increased in the presence of M-β-CD and reduced by HP-β-CD.

The results of the distribution and permeability in the presence of cyclodextrins could be applied for the modulation of the properties of the cyclodextrin-containing pharmaceutical delivery systems for the pyridinecarboxamide-based drugs.

This work was supported by the Russian Science Foundation, grant No. 22-13-00031.

THERMODYNAMIC CHARACTERISTICS OF PHASE TRANSITIONS OF BMImDCA IONIC LIQUID CONFINED IN NANO-POROUS SILICA GEL

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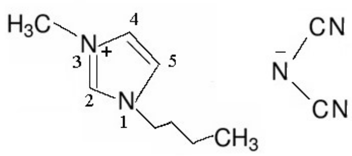
Currently, the need for efficient and inexpensive means of storing and converting energy for transport, power and industry is constantly growing. In this field, new materials based on inorganic polymer matrix and ionic liquids (ILs) have been of great interest. Such materials called ionogels (IGs) can able to retain the properties of both solid material and ionic liquids, such as high ionic conductivity and low viscosity, high chemical and thermal stability, low values of melting point, vapor pressure and flammability temperature. Therefore, ionogels can be used as quasi-solid electrolytes in various electrical devices, such as chemical current sources, fuel cells, electrochemical capacitors, etc. At the same time, under confinement condition in the solid matrix, the properties of ILs can change as a result of interaction with the host material. In this regard, for the successful use of IGs, it is necessary to study their properties.

In this work, the phase behavior of IG based on 1-butyl-3-methylimidazolium dicyanamide (BMImDCA) ionic liquid and SiO_2 as an inorganic matrix was studied. To prepare of BMImDCA/$x$$SiO_2$ ionogel, Aerosil 400 (pore size of ~ 3.3 nm) was mixed with IL in a given mass ratio and stirring for 20-30 minutes at 20 ºC until gels formed. The IGs with mass concentration x (wt. %) of 5.5, 6.5 and 7.1 were obtained. The resulting ionogels were studied by differential scanning calorimetry (DSC) in the temperature range from −120 to 100 ºC at a heating/cooling rate of 10 ºC/min in an argon flow. The glass transition temperatures (Tg) was determined during the heating cycle as the middle of the jump in the DSC curve.



It was found that the phase behavior of SiO_2-bound BMImDCA ionic liquid is similar to the phase behavior of bulk ionic liquids. During the cooling process, the ionic liquid BMImDCA, confined into silica, does not crystallize, but solidifies and then forms glass, which softens when heated, turning into a liquid state. As the SiO_2 concentration increases by 7.1 %, the glass transition temperature Tg of pure IL (−94.4 ºC) decreases by 5.1 ºC. This is explained by the hydrophilic nature of BMImDCA ionic liquid and the plasticizing effect of water. Water adsorbed on the silica surface interacts with the ionic liquid, which leads to an increase in the amorphous fraction of confined IL.

The present study shows that the ionic liquid BMImDCA confined in silica is in a pseudo-liquid phase state at lower temperatures, so the BMImDCA/$x$$SiO_2$ composites can be used as a quasi-solid electrolyte over a wide temperature range.

THERMAL STABILITY OF 1-BUTYL-3-METHYLIMIDAZOLIUM DICYANAMIDE IONIC LIQUID TRAPPED IN AN INORGANIC MATRIX SiO_2

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Ionic liquids (ILs) are salts consisting of a large organic cation and an organic or inorganic anion. They have low melting point, viscosity and volatility, high conductivity, chemical and thermal stability. Due to their unique properties, ILs are widely used in various fields of science and production, for example, to create new nanocomposite materials - ionogels, in which ILs are contained in nanopores and interparticle gaps of a polymeric organic or inorganic matrix. Such materials are promising quasi-solid electrolytes and are widely used in various electrical devices, such as chemical current sources, fuel cells, electrochemical capacitors, providing improved performance and operational reliability. However, the properties of ILs change due to the confinement effect (spatial limitation) and interaction with the confinement matrix material. Therefore, studying the properties of such materials is an urgent task.

In this work, 1-butyl-3-methylimidazolium dicyanamide (BMImDCA) was used as ionic liquid, and Aerosil 400 (average pore radius ~ 3.3 nm) was used as inorganic gelling agent. The BMImDCA/xSiO$_2$ ionogels were prepared by intensive mechanical stirring (1500 rpm) of pre-dried samples of the initial components, x – mass concentration was 5.5, 6.5, 7.1 and 8.0 wt.%. The resulting ionogels were studied by the thermogravimetric (TG) method in the temperature range from 20 and 700 ºC at a heating rate of 10 ºC/min. The decomposition temperature (T_{onset}), the peak temperature (T_{peak}) and mass loss (Δm) were determined from TG and DTG curves.

The thermal destruction of the BMImDCA/xSiO$_2$ ionogel, like the initial IL, occurs in several stages. The first weak peak observed at temperature below 100 °C is associated with the process of removing physically adsorbed water. With an increase in xSiO$_2$, the T_{onset} temperature of water evaporation and Δm_{H2O} increase by approximately 10 ºC and 3 %, respectively. This is due to the binding of H_2O molecules adsorbed on the silica surface to the confined ionic liquid. The second peak at T_{peak} temperature above 300 ºC with a sharp mass loss ($\Delta m \sim 50$ %) and subsequent weak peak about T_{peak} 400 ºC ($\Delta m \sim 20$ %) are associated with the cationic and anionic structure. The residual mass ~20 % is due to formation CN polymeric products from IL and increases with increasing xSiO$_2$ due to the contribution of the heat-resistant SiO_2 component. It was found that an increase in xSiO$_2$ by 8 %, the decomposition temperature (T_{onset}) of pure IL (293 ºC) decreases by approximately 12 ºC. This is due to the interaction of confined BMImDCA with both active groups of SiO_2 and water molecules adsorbed on the silica surface.

This study shows that the resulting BMImDCA/xSiO$_2$ composite has thermal stability close to that of the original IL, so it can be used as a quasi-solid electrolyte in the temperature range no higher than ~280 ºC.

PHYSICO-CHEMICAL STUDY OF THE DEHYDRATION PROCESSES OF *β*-CYCLODEXTRIN HYDRATES

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Cyclodextrins (CDs) are torous-like macrocycles composed of glucopyranose units, in particular *β*-cyclodextrin (*β*-CD) consists of 7 units. They have a hydrophobic inner cavity and hydrophilic ends ("rims"). This structure allows them to form inclusion complexes with a variety of organic and inorganic molecules. CDs are widely used in practice, in particular in pharmaceuticals, analytical chemistry, catalysis and in many other fields of production and science. Since the solid phase of cyclodextrins is almost always a hydrate, the process of formation of inclusion complexes is a process of complete or partial substitution of water molecules in CDs hydrates. For directional synthesis of cyclodextrin inclusion complexes in solid–gas and solid–liquid reactions, it is necessary to know the energy parameters of the hydrate water substitution processes by guest molecules. These data are insufficiently presented in the literature and are largely contradictory. The purpose of this study is to fill this gap.

Cyclodextrin hydrates of the composition *β*-CD nH$_2$O (n = 11.9-0.91) were synthesized. The obtained compounds were studied by the XRD method (Shimadzu XRD-7000), which revealed a transition from a monoclinic unit cell to an orthorhombic one with a decrease in water content. DSC investigations (Setaram Sensys DSC TG calorimeter) have found an endothermic effect in the region of 182° C, which depends on the water content in the sample.

The pressure of saturated water vapor *β*-CD 9.58H$_2$O and *β*-CD 7.0H$_2$O was measured by static method with glass membrane-gauge manometers [1] under conditions of quasi-constancy of composition. As in the case of *α*-cyclodextrin hydrates studied earlier [2-3], the water vapor pressure increases in proportion to the increase in the water content in the hydrate samples. Experimental data, reduced to a single composition *β*-CD 1.0H$_2$O, were approximated by the equation ln$p(1/T)$ which was used for calculation the thermodynamic parameters ($\Delta_{\rm pr}H^\circ_T$ and $\Delta_{\rm pr}S^\circ_T$) of the dehydration process of *β*-CD 1.0H$_2$O. The information obtained was applied to estimate the binding energy of water molecules with the *β*-CD framework.

The thermodynamic characteristics of the dehydration process were obtained for the first time and are valuable data not only for fundamental science, but also for the practical application of *β*-cyclodextrin hydrates.

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SELF-ASSEMBLY THERMODYNAMICS/KINETICS AND PHYSICOCHEMICAL PROPERTIES OF MANGANESE(III)PORPHYRIN/TETRAAZAPORPHYRIN - 4-(10-PHENYLANTHRACEN-9-YL)PYRIDINE DONOR-ACCEPTOR SYSTEMS

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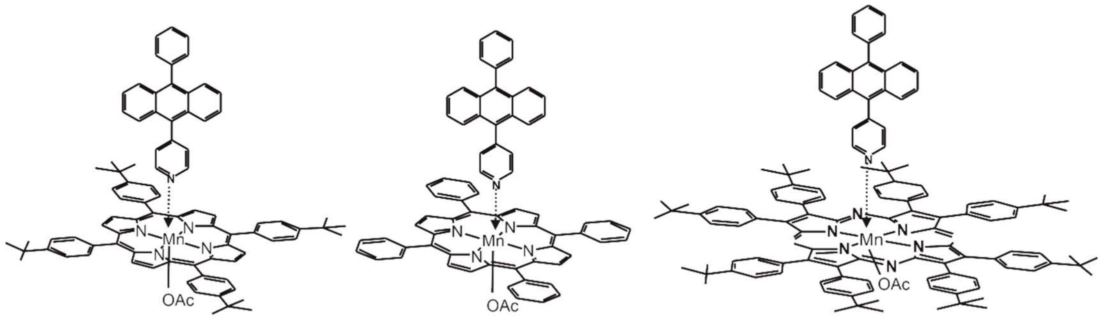
The wide application of donor-acceptor systems based on metal porphyrins and different electron acceptors contributes to the active study of their formation and thermodynamics. The anthracene-based molecules have impressive charge mobility and high solar energy conversion efficiency ascribed to the crystalline, conjugated, and planar structure of anthracene [1, 2]. We represent in this work the self-assembly of new systems based on (5,10,15,20-tetraphenylporphinato)-, (5,10,15,20-tetra-4-*tert*-butylphenylporphinato)-, (octakis(4-*tert*-butyl-phenyl)tetraazaporphinato)manganese(III) acetate and 4-(10-phenylanthracen-9-yl)pyridine (Figure) through metal-ligand axial coordination.



(AcO)(PyAn)MnTBPP (AcO)(PyAn)MnTPP (AcO)(PyAn)MnTAP

Figure. Structures of the studied dyads.

The coordination thermodynamics/kinetics was studied using fluorescence spectroscopy and mass spectrometry. It was found that the self-assembly gives 1:1 complexes (dyads) in toluene (Figure). Using ^{1}H NMR/IR/femtosecond transient absorption spectroscopy, the spectral properties and characteristics of the dyads in the ground and excited states were probed, respectively. The analysis of the lambda parameter (Λ) and the distance of hole-pair interaction (Δr-intex) by DFT/TDDFT methods has indicated the more favorable charge transfer between the tetraazaporphyrin segment of the manganese(III) complex and the axial PyAn fragment. The data obtained develop the fundamental basis for the application of manganese porphyrin-anthracene systems in photovoltaics.

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MAGNETIZATION THERMODYNAMICS OF PARAMAGNETIC D-METAL PORPHYRIN COMPLEXES

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Porphyrin complexes of metals with outer unpaired *d*/*f* electrons are studied as SMMs at the temperatures below the T_{Curie} (up to 50 K) [1]. Being paramagnetic at the temperatures close to room, they display magnetocaloric effect (MCE) achieving “large” and even “giant” values [2]. Such magnetocaloric compounds are of great interest for both magnetic cooling in technology and everyday life and hyperthermia in medicine.

The direct measurement of room temperature MCE using the original microcalorimetric method together with DSC one makes it possible to determine the thermodynamic parameters of magnetizations for porphyrin-based paramagnets. We represent here the results on thermodynamics of magnetization for porphyrin complexes with manganese(III) and molybdenum(V) having $3d^4$ and $4d^1$ electronic configuration, respectively. The paramagnetic porphyrin complexes with the set of both axial ligands and macrocycle substitutients were synthesized. The UV-vis, IR, ^{1}H NMR, and MALDI TOF spectral method were used for the chemical structure conformation. The heat, the enthalpy, the entropy change, and the heat capacity (Q_{MCE}, ΔH, ΔS, and C_p respectively) and MCE when exposed to magnetic fields from zero to 1 T were obtained for the polycrystalline samples of porphyrin complexes. The effects of structural modification in the MCE value were revealed, and the temperature/field dependencies of the thermodynamic parameters (Figure) were used for the MCE origin determination.

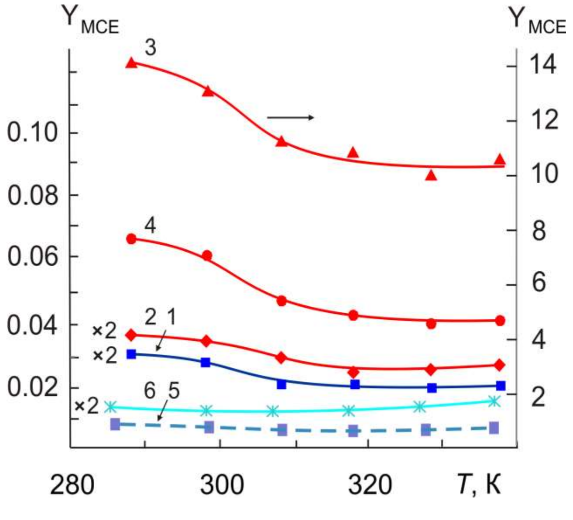

Figure. The temperature dependences of the magnetization thermodynamic parameters for O=Mo(OEt)TPP (1, 2, 3, 4) and (Cl)MnOEP (5, 6) at the magnetic field 1.0 T. Y_{MCE}: ΔT_{MCE}, K (1, 5), Q_{MCE}/m, J/g (2, 6), -ΔH_{MCE}, J/mol (3), and -ΔS_{MCE} J/(kg K) (4)

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This work was supported by the Russian Science Foundation (Project number no. 21-73-20090). We are grateful to the center of the scientific equipment collective use «The upper Volga region center of physico-chemical research».

VAPOR PHASE AND HETEROGENEOUS EQUILIBRIA IN THE Ga – I (Ga – Cl) SYSTEMS ACCORDING TO THE HT-SPECTROPHOTOMETRIC DATA

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The equilibria involving gallium halides can be used for the tasks of chemical vapor transport (CVT) – both in their classical ways, associated with the chemical sublimation and recrystallization of the required solids via the gas-phase, and in the selective transport version, in which the non-stoichiometric composition of a solid is regulated without its recrystallization [1]. Here we analyse the UV- and vis- absorption spectra (200 – 800 nm) of gallium chlorides and iodides vapor at some homogeneous and heterogeneous equilibria, obtained *in situ* at temperatures from 200 to 900 °C The experiments was carried out on a spectrophotometric device mounted on the basis of an MDR-41 monochromator. Equilibrium was organized in the evacuated and sealed quartz cuvettes, which in the experiments were placed in a tubular electric furnace equipped with through windows for the passage of light. By analysing the obtained spectra, the main absorption characteristics were obtained for various molecular species of gallium halides.

These results have already been partially presented for the Ga – I system in ref. [2], and in this study these data are refined. In addition, in this study, considerable attention is paid to the analysis of stationary states that arise during the realisation of heterogeneous equilibria under non-isothermal conditions: for example, when the equilibrium (1) is realized in different parts of the ampoule at different temperatures.

$$2\mathrm{Ga}'' + \mathrm{GaI}_3' = 3\mathrm{GaI}' \qquad (1)$$

In Eq. 1 Ga″ stands for the gallium that is included in the composition of some gallium-containing condensed phases, and GaI_3' and GaI′ are the components of the vapor phase.
Using the example of equilibrium (1), the results of an experimental verification of the stationarity condition (2), derived for non-isothermal gas transport systems, are also analyzed.

$$K_P^{\#}(T_2, x_2) = K_P^{\#}(T_1, x_1), \qquad (2).$$

where $K_P^{\#}(T_i, x_i)$ (i = 1; 2) is a value, which is similar to the heterogeneous equilibrium constant, relating the partial vapor pressures in Eq. (1):

$$K_P^{\#}(T_i, x_i) = p_{\mathrm{GaI}}^3 \Big/ p_{\mathrm{GaI_3}} \,. \qquad (3)$$

Finally, T_i (i = 1; 2) are the temperatures of different zones, and *xi* are the compositions of the Ga-containing condensed phases.

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ENTHALPY OF SUBLIMATION OF VO-ETIOP-III PETROPORPHYRIN

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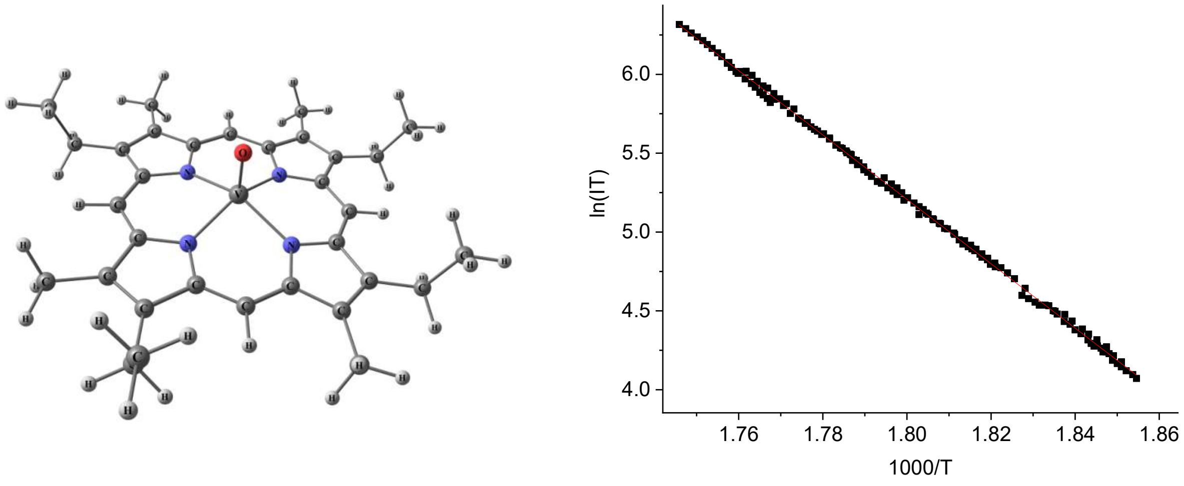
Thermodynamic parameters of petroporphyrins are important from the viewpoint of crude oil processing and their possible further use. Here we examine the sublimation ability of a typical petroporphyrin, oxovanadium etioporphyrin-III, VO-EtioP-III – Figure 1. Its chemical structure, electronic and solid-state properties were studied earlier [1].



a b

Figure 1. (a) Molecular structure of VO-EtioP-III. (b) Dependence of the molecular ion intensity logarithm of VO-EtioP-III on temperature

The mass spectrometric study of the process of sublimation of VO-EtioP-III by the Knudsen method was carried out using the MI-1201 magnetic sector mass spectrometer modified for thermodynamic studies. The most intensive peak (m/z = 543 a.m.u.) in the electron impact mass-spectrum of VO-EtioP-III recorded at 570 K corresponds to a molecular ion $[M]^+$ [1].

The sublimation enthalpy for VO-EtioP-III was estimated by the molecular ion intensity measurement through the gradual increase of the cell temperature from 538 to 573 K. The Figure 2 shows the ln(IT) = f(1000/T) dependence for molecular $[M]^+$ ion. In this coordinates, the experimentally obtained points form a straight line with correlation coefficient R=0.999. Each point of the plot corresponds to the ion current measured after its stabilization at a given temperature. The enthalpy of sublimation value ΔH_s calculated by linear regression using the Clausius–Clapeyron relation was found to be equal to 170 (5) kJ*mol^{-1}. The value of ΔH_s is similar to the data for related compounds [2]

[1] Pakhomov, G.L., et al., *ChemistrySelect*, 2023, 8, e202303271.
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THERMODYNAMIC CHARACTERISTICS OF THE FORMATION OF ALLOYS OF REE WITH LIGHT NON-FERROUS METALS

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The data on thermodynamic characteristics of chemical reactions allow to choose the right conditions for the technological process of their carrying out, as well as to estimate the possibility of spontaneous reaction under standard conditions.

High-temperature exchange reactions involving compounds of rare-earth elements (REE) and reducing metals can be used as an alternative way to produce alloys and ligatures based on these metals [1].

We carried out refining thermodynamic calculations using available literature data on enthalpies of alloy formation of intermetallic compounds (IMC), for systems based on aluminium and magnesium, containing REE of cerium subgroup, as well as calculations of equilibrium constants of high-temperature exchange reactions of IMC formation in order to determine the most probable form of IMC.

It is expedient to obtain alloys based on aluminium and magnesium from REE fluorides because the Gibbs energies of REE fluorides formation are 1.6-1.7 times lower than those of REE chlorides. For aluminium and magnesium fluorides and chlorides this difference is 1.8-2.2 times. The formation energy significantly affects the calculation of thermodynamic characteristics of high-temperature exchange reactions.

Calculation of equilibrium constants of high-temperature exchange reactions showed that for aluminium-based systems the formation of IMCs of $Al_{11}Ln_3$ composition is most likely. For magnesium-based systems, IMCs of the composition $Mg_{17}Ln_2$ for lanthanum and europium most likely and IMCs compositition $Mg_{41}Ln_5$ for cerium, praseodymium, neodymium, and samarium are formed.

Introduction of excessive amount of sodium fluoride into the system to form complex compounds of Na_3LnF_6 type allows to shift the electrode potential of the system to a more electronegative region, which leads to the formation of IMCs richer in REE content. IMCs decompose by peritectic reactions into compounds with lower and higher REE content.

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INTERACTIONS IN MIXTURES OF CHOLINE CHLORIDE WITH UREA, FORMAMIDE, ETHANOLAMINE AND 1-AMINO-2-PROPANOL OF COMPOSITION 1:2 ACCORDING TO QUANTUM CHEMICAL CALCULATIONS

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It is known that deep eutectic solvents (DES) represent a class of potentially environmentally friendly solvents that exhibit useful properties in various technological processes such as extraction, sorption, petroleum product refining and much more. Recently, amine-containing DES have received much attention as they are considered to be effective absorbers of greenhouse gases, particularly carbon dioxide. Therefore, before proceeding to study the mechanisms of CO_2 uptake, it is necessary to focus on the characteristics of the interactions between the DES components. Choline chloride is a known hydrogen bond acceptor (HBA), and urea, formamide, ethanolamine, and 1-amino-2-propanol are good H-bond donors (HBD).

Quantum chemical calculations were carried out for various structures of complexes of choline chloride with two molecules of urea, formamide, ethanolamine and 1-amino-2-propanol. Calculations were performed in the Gaussian 16 software package by the density functional method (DFT) using the B3LYP functional with the GD3 dispersion correction and the 6–311++g(2d,2p) basis set to take into account various types of interactions. All structures do not have imaginary frequencies, which confirms their stability. The electron density and potential energy density at critical points calculated within the QTAIM theory are proportional to the interaction energy. The interaction energies were calculated for all particles in the complex by counterpoise method, taking into account charges, and for neutral particles of choline chloride with molecules of urea, formamide, ethanolamine and 1-amino-2-propanol. The relatively small value of the BSSE correction indicates the choice of a sufficiently large basis to describe the system. The dispersion interaction energy was calculated as the energy difference with and without the GD3 dispersion correction. Coulomb interactions were calculated in the Multiwfn package as the difference between the Coulomb energies of the complex and its components. The free energies of complex formation were calculated, as the difference between the free energies of the complex and its components.

Quantum chemical calculations indicate the presence of various interactions between the components in these systems, including H-bonds, both O-H...Cl and N-H...Cl, and also C-H...O, C-H...Cl, C-H...N, as well as Coulomb and dispersion interactions. The most stable complexes are formed due to hydrogen bonds with the chloride ion. For amino alcohols, it has been shown that more stable complexes are formed in the case of O-H...Cl bonds. The main contribution is made by Coulomb interactions, due to the presence of charged particles in complexes (cations and anions). It is also shown that dispersion interactions play a significant role. The energies of various bonds were estimated. There are linear correlations between interaction energies and free energies of complex formation.

The study was supported by the Russian Science Foundation grant No. 23-13-00118, https://rscf.ru/project/23-13-00118/

SUPRAMOLECULAR SYSTEMS OF *meso*-SUBSTITUTED COBALT(II) PORPHYRINS WITH FULLERENES C_{60}/C_{70}: SELF-ASSEMBLY AND SPECTRAL PROPERTIES

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The combination of cobalt porphyrin complexes with graphenes [1], nanotubes [2], and fullerenes [3] into molecular systems makes it possible to obtain new properties that are necessary for the development of photocatalysts and components for photovoltaic devices.

The report represents thermodynamic/kinetic data on the processes of self-assembly of donor-acceptor complexes based on cobalt porphyrins and fullero[60]/[70]pyrrolidines (Ful). The influence of macrocycle substituents on the composition of the resulting molecular systems, on the values of formation rate constants, and stability is shown. It was found that the formation of axially coordinated 2: 1 complexes $(Ful)_2CoP$ is more characteristic for this reaction. However, in the case of interaction of first and second generation carbazole-containing porphyrins with 2,5-di(pyridin-2'-yl)-3,4-fullero[70]pyrrolidine (Figure), the complex of composition 1: 1 is formed.

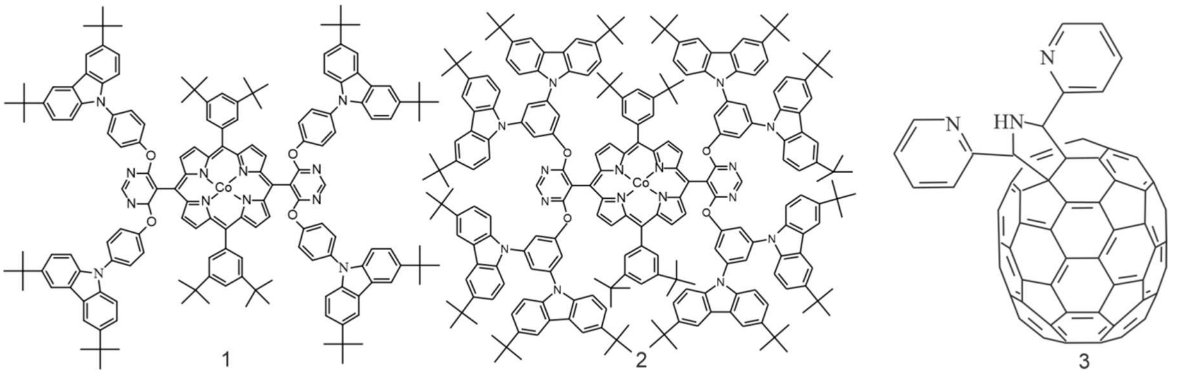

Figure. The structural formulas of carbazole-containing cobalt(II)porphyrins (1, 2) and 2,5-di(pyridin-2'-yl)-3,4-fullero[70]pyrrolidine (3).

IR, NMR and mass spectra that confirm the formation of axial complexes were obtained for donor-acceptor systems. The correlation between the thermodynamic formation parameters and the structure of axial complexes is found.

[1] J.-M. You, H.S. Han, H.K. Lee, S. Cho, S. Jeon, *Int. J. Hydrogen Energy*, 2014, 39, 4803.
[2] S. Dou, L. Sun, S. Xi, X. Li, T. Su, H.J. Fan, X. Wang, *ChemSusChem*, 14, 2021, 2126.
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PORPHYRIN COMPLEXES OF COBALT, RHODIUM AND IRIDIUM AS THE PRECURSORS FOR INTERMEDIATES OF CATALYTIC PROCESSES

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The catalytic properties of the cobalt subgroup porphyrin complexes successfully ensure organic substrate transformations associated with the activation of bonds in them, often considered as kinetically inert [1]. From applying point of view, this is necessary for cracking processes, CO oxidation, etc., which contribute to the efficient use of organic raw materials and improving the environment. The mechanism of the reactions based on partial or complete intra- and/or intermolecular electron transfer, usually involves the molecules activation through coordination at the central metal in metalloporphyrin. For developing using strategies and directly implementing the capacity of the compounds we report on the study of the systems based on porphyrin complexes of cobalt, rhodium and iridium possessing the stability in solutions that is enough for detailed investigation by spectroscopy techniques.

The donor–acceptor self-organizating system (5,10,15,20-tetraphenyl-21H,23H-porphyrinato)cobalt(II) (CoTPP)–1-methyl-2-(pyridin-4'-yl)-3,4-fullero[60]pyrrolidine (PyC_{60}), $(PyC_{60})_2CoTPP$, was studied using UV-vis, IR, and (^1H, ^{13}C)NMR spectroscopy, chemical kinetics and thermodynamics. The photoelectrochemical characteristics (photocurrent density and IPCE) of the $Ti|TiO_2$ electrode modified by the triad and its precursors were determined and the redox behavior of the latter was studied by cyclic voltammetry in dichloromethane.

For the isostructural complexes of rhodium(III) and iridium(III) with H_2TPP the chemical generation of oxidized species occurring due to the interaction of the coordination center with atmospheric molecular O_2 with the assistance of protons in aerated HOAc, H_2SO_4, CF_3COOH and HOAc–H_2SO_4 mixtures was studied. The oxidation was shown to be preceded by an axial substitution reaction with ions and molecules of the reaction medium. The actual site of electron transfer is found out to depend on the central cation and acidity of the mixed solvent (for $Ir^{III}P$).

In 100% AcOH, π-cation radical species $(HOAc)(AcO)Ir^{III}TPP^{\bullet+}$ is slowly formed; in CF_3COOH the oxidation of the central metal ion occurs affording the iridium(IV) species $(CF_3COO)_2Ir^{IV}TPP$; in concentrated H_2SO_4 Ir(III)→Ir(IV) transition takes place followed by oxidation on aromatic part of the molecule up to $(HSO_4)_2Ir^{IV}TPP^{\bullet+}$.

Unlike the iridium complex, (Cl)RhTPP in the solvents of different acidity (H_2SO_4/HOAc and concentrated aqueous H_2SO_4) forms the same species with positive charge localized at the aromatic part while the metal oxidation state remains the same Rh^{+3}. The higher stability of (Cl)RhTPP in chemical oxidation in aerated acids compared to the iridium counterpart is explained by the more effective participation of the rhodium atom in π-interaction with the macrocycle due to its higher electronegativity in comparison with Ir^{+3}, as well as its lower reactivity in axial substitution reactions. The results obtained are in accordance with the oxidation potentials for iridium and rhodium porphyrins, corresponding to the electrochemical generation of one- and two-oxidized species, as well as their FMO energies [2].

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THE STABILITY OF N-BUTYL ALCOHOL UNDER TEMPERATURE

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Biobutanol made from biomass is butyl alcohol, which can be used as biofuel or bio component of fuel. This type of fuel has high potential and can be used in carburetor and injector internal combustion engines pure or blended with other fuels [1].

Many works have been devoted to studies of the thermal stability of liquid substances, including representatives of the class of aliphatic alcohols (methanol, ethanol, n-propanol) [2]. Unfortunately, among the works studied only one is devoted to the study of thermal decomposition of butyl alcohol. The authors of this work investigated the products of alcohol decomposition [3]. They are formaldehyde, carbon monoxide, methane and hydrogen, also ethane, ethylene, propane and propene were found in small amounts.

The paper presents the results of an experimental study of the persistence of n-butyl alcohol under the influence of temperature. The temperature of the beginning of thermal decomposition Td of n-butyl alcohol molecules and the rate of thermal decomposition of its molecules depending on the density ρ and temperature T were estimated. As a value proving the presence of decomposition of butyl alcohol molecules, we used the value of pressure and refractive index, the measurements of which before and after exposure to temperature were carried out on the refractometer IRF - 22. Changes in the composition of the studied sample could be observed by color.

Table. Values of temperatures of the beginning of decomposition (Td) and values of refractive index (n) before and after heat treatment

Sample	Td, *K*	Pressure *ΔP, MPa*	Exposure time, hours	Pressure, *MPa*	*n,* before decomposition	*n,* after decomposition
N-butanol	558.15±1	0.052	48	5.09±0.02	1.399	1.394

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[3] J.A. Barnard and H.W.D. Hughes, *Trans. Faraday Soc.*, 1957, 53, 1423.

THERMAL AND TRANSPORT PROPERTIES OF IONIC LIQUIDS FORMED BY METHYLPROPYLAMMONIUM CATION AND SULFONIC ACID ANIONS

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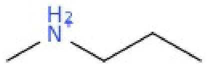
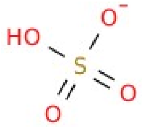
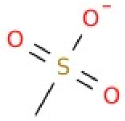
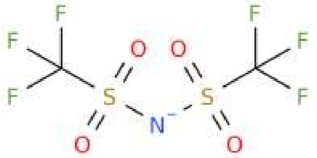
Protic ionic liquids (PILs) are organic salts with melting temperatures below 100°C. PILs are a subclass of ionic liquids which contain “active” (mobile) protons in the structures. They also possess a number of properties important for their practical use such as low vapor pressure, wide temperature range of the liquid state, large electrochemical window, high thermal stability and electrical conductivity and so on. Therefore PILs are being actively studied as potential dopants for proton-conducting membranes.

Here we present the data on the properties of three protic ionic liquids composed of the same cation, methylpropylammonium (MPA), and different anions (hydrogen sulfate (HSO_4^-), mesylate (MsO) and bis(trifluoromethanesulfonyl)imide (TFSI)):

MPA	HSO_4^-	MsO	TFSI
			

First of all, the thermal properties of the PILs were investigated. TG analysis was conducted to determine the membrane decomposition temperatures. All the PILs are thermally stable up to 250°C at least.Their t_{dec}^{onset}values increase in the series: [MPA/HSO_4] (pKa=-2.8) <[MPA/MsO] (pKa=-1.9)<[MPA/TFSI] (pKa=0.155). DSC method was applied to measure the phase transition temperatures. The melting temperatures (T max) of the [MPA/MsO], [MPA/TFSI] and [MPA/HSO_4] are equal to 1, 13 and 63°C, respectively.

The PIL conductivity was calculated from its resistance.The bulk resistance of the PILs was measured using the electrochemical impedance spectroscopy method in a measuring cell with platinum electrodes. The PILs conductivity increases with the temperature rising and reaches 39mS/cm ([MPA/TFSI]), 46 mS/cm ([MPA/MsO]), and 85 mS/cm ([MPA/HSO_4]) at 145°C. The resulting temperature dependences were fitted with the Arrhenius equation and the conductivity activation energies were calculated for each PIL.

SPECTRAL PROPERTIES OF SUPRAMOLECULAR COMPLEXES BASED ON CYCLODEXTRIN AND 5,10,15,20-TETRAPHENYLPORPHYRIN

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Model systems of "host-guest" inclusion complexes based on β-cyclodextrin (β-CD) and 5,10,15,20-tetraphenylporphyrin (TPP) in aqua-organic mixture (aqua/N,N-dimethylformamide, DMF) were obtained and investigated using optical absorption and spectrofluorimetry methods.

Conclusions were made about the successful synthesis of such supramolecular systems. The obtained data indicate a change in the absorption intensity of the system β-CD – TPP depending on the change in the concentration of TPP in the solution. There is a slight shift by 1 nm of the maximum absorption for all systems of β-CD – TPP – aqua – DMF depending on the concentration of TPP solution in DMF, which indicates the formation of a host-guest complex. Fluorescence spectra of the β-CD – TPP – aqua – DMF system with different concentrations of TPP and β-CD also show a change in fluorescence intensity depending on the concentrations of TPP and β-CD in the system. The results of spectral studies confirm the formation of supramolecular complexes β-CD – TPP, in which molecules of both substances are connected by weak non-covalent interaction.

Using the mathematical analysis methods, changes in the spectral properties of the chromophore were analyzed.

These complexes may be useful when developing targeted drug delivery systems for photodynamic therapy and diagnostics.

This work was supported by the IBCP RAS State Targets Project # 122041400110-4 and was carried out within the framework of the project "Research on the problems of disposal of waste of natural origin for the practical use of the obtained products"(122122600056-9).

SPECTRAL FEATURES OF INTERACTION OF HEMIN AND ZINC PORPHYRIN WITH SODIUM HEXAMOLYBDENICELATE

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The interaction of hemin (Fe (III) -complex with protoporphyrin IX, FePP) and the Zn (II) -complex of tetra (4-pyridyl) porphyrin (ZnTPP) with hexamolibdenonicelate - anions (sodium hexamolybdenonicelate crystalline hydrate $Na_4[Ni(OH)_6Mo_6O_{18}]\cdot 8H_2O$, HMN) in an aqueous – organic medium was investigated using optical absorption and fluorescence methods. N,N-dimethylformamide (DMF) was used as an organic solvent.

Comparison of the absorption spectra of individual compounds and their mixtures shows that co-presence of organic and inorganic components in binary solution leads to formation of hybrid structures (complexes). In the electron absorption spectra of the mixture of FePP and HMN in aqueous – organic medium, a new band is manifested that is not the characteristic of pure FePP). A similar effect is not found when FePP is transferred to an aqueous medium from DMF. The spectral behavior of ZnTPP reflects its presence mainly in monomeric form in complex with HMN, while in aqua ZnTPP is represented by molecular aggregates. In addition, in complexes with HMN, the fluorescence of ZnTPP is extinguished, which appears to occur by the mechanism of electron transfer from porphyrin in HMN.

The binding ability of systems was evaluated, as well as the stability of the resulting hybrid complexes.

Studies carried out in this research field will significantly expand the range of applications of hybrid organo-inorganic systems based on porphyrins and heteropoly compounds due to their stabilization in aqueous environments.

This work was supported by the IBCP RAS State Targets Project # 122041400110-4 and was carried out within the framework of the project "Research on the problems of disposal of waste of natural origin for the practical use of the obtained products"(122122600056-9).

PRACTICAL JUSTIFICATION OF THERMOCHEMICAL CALCULATIONS IN THE INTERPRETATION OF MASS SPECTROMETRIC DECAY USING THE EXAMPLE OF A DERIVATIVE OF THE ALKALOID LAPPACONITINE

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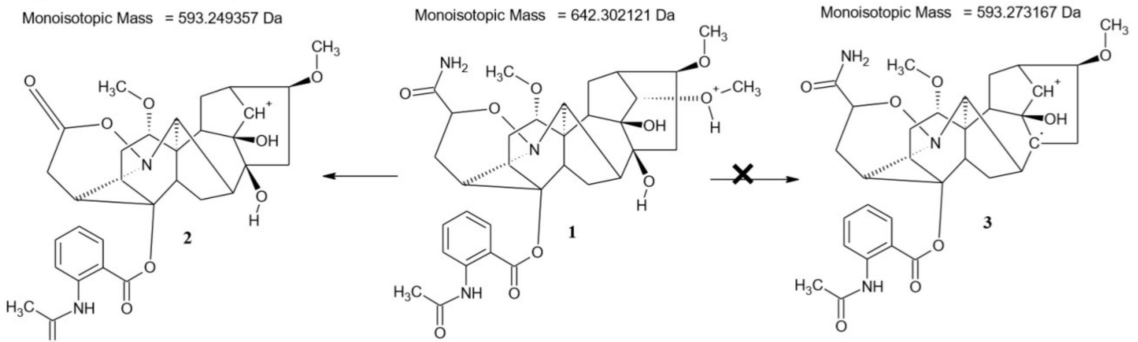
Due to the great complexity of hardware interpretation of real mass spectra from available databases, it is advisable to carry out preliminary thermochemical calculations to simplify the analysis and increase the accuracy of the results. The fragmentary mass spectrum of the lappaconitin alkaloid derivative **1**, in addition to the peak of the $[M+H]^+$ ion with m/z 642.3006, contains a peak of the fragmentation ion with m/z 593.2449, in connection with which this ion is characterized by structure **2**, formed by separation from the [M+H]+ ion of methanol and ammonia molecules, unlike structure **3**, which is formed by cleavage of a methanol molecule and an -OH group. This confirms thermochemical calculations of the total energy for both structures, according to which the formation of the first structure is energetically more likely (the value of the total energy of ion **2** is 0.3 eV less than the total energy of structure **3**).



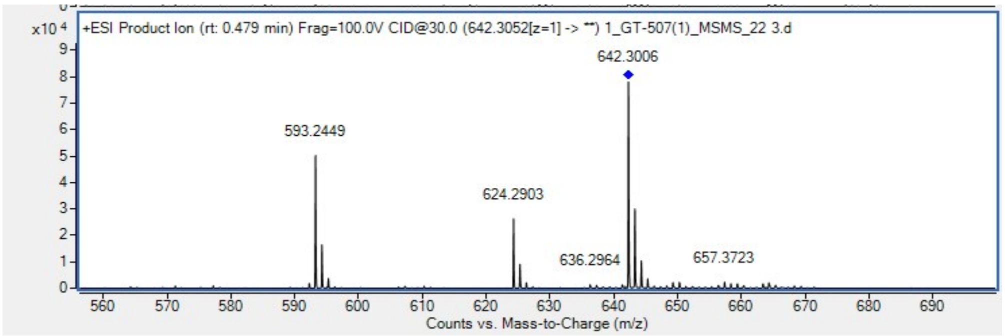


Figure 1. High-resolution mass spectrum of the lappaconitin derivative.

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ELUCIDATION OF BICALUTAMIDE CONFORMERS IN DMSO-D6: A COMBINED NMR AND COMPUTATIONAL STUDY

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Compounds that can exist in various polymorphic forms are fascinating to the pharmaceutical industry. This is because they can be modified to create materials with desired properties. Polymorphism can be a problem for pharmaceuticals because different forms of a compound can have significant differences in their physical and pharmaceutical characteristics. Therefore, detecting, controlling, and minimizing the likelihood of obtaining an unstable or metastable form when creating medicinal compounds is essential. Some medicinal compounds have different forms caused by different conformations of molecules in the crystal's unit cell. To predict the resulting polymorphic form, it is necessary to determine and monitor the conformational equilibria of small molecules of drug compounds in solutions [2,3]. In this work, using nuclear magnetic resonance (NMR) spectroscopy techniques, we analyzed the spatial structure of the antiandrogenic compound used to treat prostate cancer - bicalutamide.

With its established efficacy, bicalutamide also presents a range of side effects, including gynecomastia, which can lead to irreversible hyalinization, fibrosis, and tissue necrosis. This underscores the importance of our research in finding ways to modify the forms of bicalutamide. During our study, we recorded and interpreted NMR spectra (^{1}H, ^{13}C, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H TOCSY, and ^{1}H-^{1}H NOESY) of bicalutamide in deuterated dimethyl sulfoxide (DMSO-d6). We also performed quantum chemical calculations within the density functional theory (DFT) framework to determine the structures of the conformers of bicalutamide molecules. By using nuclear Overhauser effect spectroscopy data, we were able to measure internuclear distances that indicated changes in the molecular structure of the object under study. This helped us determine the ratios of bicalutamide conformer groups in DMSO-d6. These findings will significantly aid in the ongoing efforts to modify the forms of bicalutamide, enhance its properties, and reduce its side effects.

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THERMODYNAMIC DESCRIPTION OF LIQUID CRYSTALLINE N(p-ALKYLOXYBENZYLIDEN)-p-TOLUIDINES – ORGANIC SOLVENT SYSTEMS

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N(p-alkyloxybenzylidene)-p'-toluidines R-O-C_6H_4-CH=N-C_6H_4-CH_3 (where R = C_4H_9, C_9H_{19}, $C_{10}H_{21}$) were studied as mesogens. The temperatures of phase transitions of individual liquid crystals (LC) were obtained by DTA and polarization microscopy. The purity of the mesogens was evaluated by cryoscopy, and the total impurity content did not exceed 1 mol %.

The solubility polytherms were studied with organic solvents of different polarity: alkanes (n-C_6H_{14}, n-C_7H_{16}), cycloalkanes (C_6H_{12}, C_6H_{11}-CH_3), aromatic compounds (C_6H_6, p-$C_6H_4(CH_3)_2$), alcohols (C_2H_5OH, propan-1-ol).

All the systems studied are shown to get greater the solution enthalpy figures than the fusion enthalpy ones (the data obtained for $C_{10}H_{21}$-O-C_6H_4-CH=N-C_6H_4-CH_3 LC are shown in Table 1). For alkanes and alcohols, Δ_sH^o decreases with increasing mesogene alkyl chain length. The mesogens studied demonstrate better dissolution in aromatic solvents than in alkanes and alcohols, while alkanes and alcohols are traditionally used as solvents for recrystallization.

Table 1. Solution Enthalpies for N(*p*-n-decyloxybenzyliden)-*p*'-toluidene (Δ_sH^o - solution enthalpy, R^2 - correlation coefficient)

liquid crystal material	solvent	a	b	R^2	Δ_sH^o, kJ/mol
N(*p*-n-decyloxybenzyliden)-*p*'-toluidene	n-hexane	19,915	-7317,1	0,9843	60,8±3,6
	n-heptane	18,51	-6855,5	0,9912	57,0±3,4
	benzene	16,82	-5671,7	0,9989	47,2±1,1
	p-xylene	13,71	-4792,5	0,9906	39,8±3,4
	ethanol	17,30	-7116,9	0,9856	59,2±5,0
	propan-1-ol	12,79	-5563,3	0,9901	46,3±3,0
	cyclohexane	23,915	-8156,8	0,9964	67,8±2,5
	methylcyclohexane	24,21	-8314,1	0,9946	69,1±2,9

The excess Gibbs energy was estimated using the solubility parameters within the framework of the regular solution model (where V_1 is a volume of LC, φ_2 is the volume fraction of solvent):

$$G_1^E = V_1\varphi_2^2(\delta_1 - \delta_2)^2$$

SOLUTIONS OF WATER AND UREA IN TERTIARY BUTYLAMINE: THE PHENOMENON OF "THERMOACTIVATED PARTIAL ISOBARIC COMPACTION OF THE SOLUTE" ACCORDING TO DENSITY MEASUREMENTS BETWEEN 278.15 AND 303.15 K

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Based on the precision data on density of dilute solutions of water (W) and urea (U) in *tert*-butylamine (TBA), the phenomenon of *thermoactivated partial isobaric compaction of a solute structure* connected with the negative standard molar expansibility of W or U, $E_{p,2}^{\circ} = (\partial V_2^{\circ}/\partial T)_p$, in this amine was discovered. The results are given in Table 1 and Fig. 1 [1,2].

Table 1. Molar volumes of components (V_{W}^*, V_{U}^* and V_{TBA}^*, in cm^3·mol^{-1}), standard molar volumes of solutes (V_{W}° and V_{U}°, in cm^3·mol^{-1}) in TBA and *relative affinity parameters* ($\Delta G^{*,\circ}$, in kJ·mol^{-1}) for the compared binary systems at different temperatures, *T*/ K, and *p* = 0.1 MPa

T/ K	V_{W}^*	$V_{\mathrm{W}}^{\circ}(=\bar{V}_{\mathrm{W}}^{\infty})$	V_{U}^*	$V_{\mathrm{U}}^{\circ}(=\bar{V}_{\mathrm{U}}^{\infty})$	V_{TBA}^*	$\Delta G^{(*),\circ}$(W)	$\Delta G^{(*),\circ}$(U)
278.15	18.016	9.41	45.03	26.29	103.27	–2.10	–1.72
283.15	18.021	9.27	45.08	25.18	104.04	–2.15	–1.78
288.15	18.031	9.08	45.13	23.76	104.83	–2.19	–1.85
293.15	18.048	8.96	45.19	22.41	105.64	–2.23	–1.92
298.15	18.068	8.82	45.26	21.06	106.47	–2.27	–1.99
303.15	18.094	8.68	45.34	19.69	107.33	–2.32	–2.06

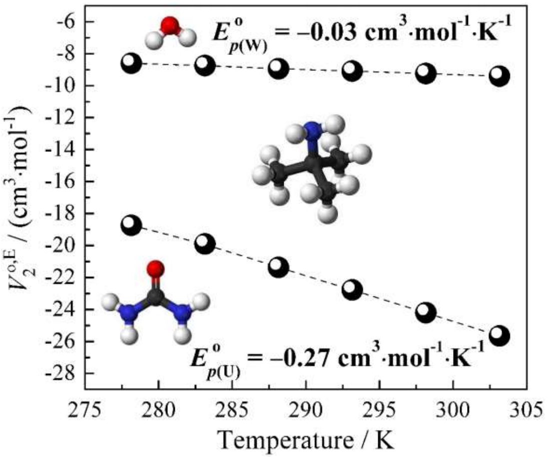

Figure 1. Temperature dependences of standard excess molar volumes or volumetric effects of dissolution [1,2], $V_2^{\circ,\mathrm{E}} = V_2^{\circ} - V_2^*$ (see Table 1), for water and urea as solute species in *tert*-butylamine (a molecule located in the figure center). The total uncertainty (a confidence level is 0.95) in determining the values depicted does not exceed 0.2 cm^3·mol^{-1}, at worst (in the case of standard solution of U in TBA).

According to Ben-Naim's approach based on the *relative affinity parameter*, $\Delta G^{(*),\circ} = RT(V_2^{\circ} - V_1^*)/V_1^* = RT(G_{11}^{(*),\circ} - G_{12}^{(*),\circ})/V_1^*$ [1,2]. In our case, $\Delta G^{(*),\circ} < 0$ (Table 1) because the Kirkwood-Buff integral $G_{11}^{(*),\circ}$ is smaller than that of $G_{12}^{(*),\circ}$. Thus, due to increasing $\Delta G^{(*),\circ}$ in magnitude, the structure packing of TBA in the solvation sphere of W or U becomes decreasingly expansible compared to the solvent structure *in bulk*, as the temperature is rising.

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THERMODYNAMIC ANALYSIS OF LIQUID CRYSTALLINE PHENYLBENZOATE – SOLVENT SYSTEMS

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Phenyl benzoates (PhBz) is a traditional class of liquid crystals (LC). To expand the field of practical application, it is necessary to have information concerning the nature of intermolecular interactions in LC systems and in LC – solvent systems.

Nematic phenyl benzoates ($p\text{-}R_1\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}R_2$: H-70, $R_1 = OC_6H_{13}$, $R_2 = OC_4H_9$; H-73, $R_1 = OC_6H_{13}$, $R_2 = OC_7H_{15}$; H-93, $R_1 = OC_4H_9$, $R_2 = OC_6H_{13}$) were used. Solubility curves for selected PhBz in solvents of different classes were obtained. The results are presented in the form of dependencies $-\ln x_1 = a - b/T$, $b = \Delta_sH^o/R$, where x_1 is the molar fraction of LC in saturated solution at temperature T [K], R is the universal gas constant, Δ_sH^o is the enthalpy of solution. As an example, we present the data for H-73 (Figure 1).

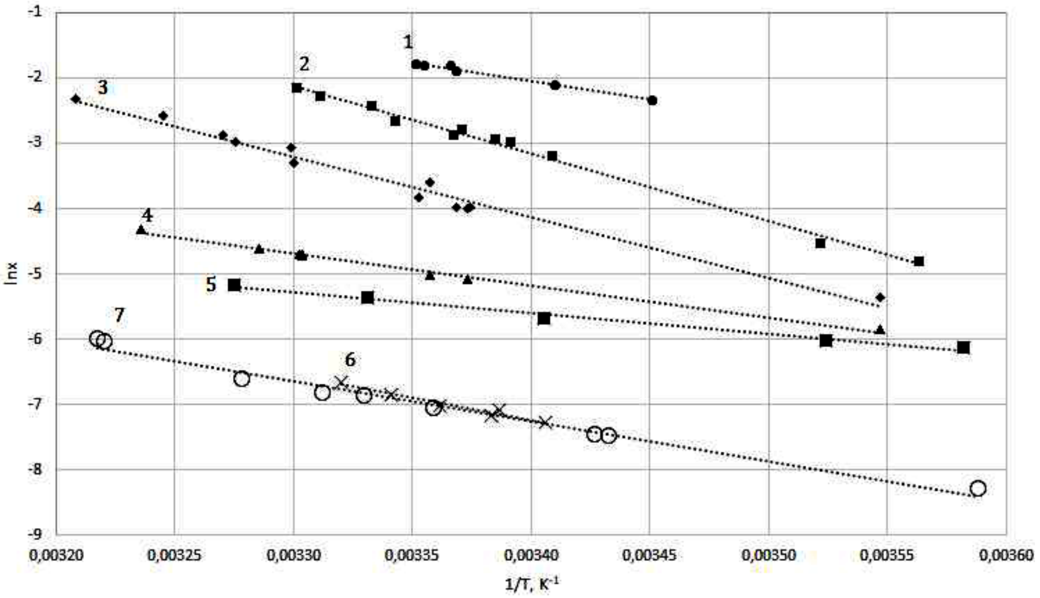

Figure 1. Solubility of H-73. Solvents: 1 – 1,4-dioxane; 2 – cyclohexane; 3 – n-heptane; 4 – 2-propanol; 5 – 1-propanol; 6 – ethanol; 7 – methanol

Positive deviations from ideality are observed in all systems ($\Delta_sH^o > \Delta_{fus}H^o$). Solubility was calculated using the Hansen solubility parameters (δ_{di}, δ_{pi}, δ_{hi}). Based on the data obtained, the solubility of LC at 298 K was analyzed using the reduced radius R_a [1]:

$$R_a^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 ,$$

where δ_{d1}, δ_{p1}, δ_{h1} are the solubility parameters of LC, δ_{d2}, δ_{p2}, δ_{h2} are the solubility parameters of solvent.

It was found that the lowest values of R_a were in 1,4-dioxane and in cyclohexane, which confirmed good solubility in these solvents. The excess thermodynamic functions were calculated.

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STUDY OF THE GLYCEROL SORPTION CAPACITY OF ZEOLITE CATALYSTS BY THERMAL ANALYSIS AND CALORIMETRY

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Biomass is a rich source of renewable carbon, which can be converted using a range of technologies into environmentally friendly fuels and chemicals. An important environmental problem is the large amount of waste in the production of biodiesel. Utilization of glycerol, the main by-product (about 10 wt.%) of bio-diesel industry, with its conversion to products with high added value, is currently an urgent task in the direction of green, energy-saving and low-carbon development in the field of atmospheric ecology and the development of bioenergy. In this regard, effective methods of increasing conversion (dehydration, carboxylation and other processes) are highly required. Both the effectiveness of glycerol conversion and its selectivity are determined by a catalyst and its sorption capacity in respect to glycerol.

In this contribution we report the results of our study of glycerol sorption by various microporous and mesoporous zeolite-based catalysts modified with transitional metals probed by methods of thermal analysis (TG/DSC of desorption, Netzsch STA 449 F1) and isothermal calorimetry of sorption (Setaram C80). A comparative analysis is focused on the role of zeolite topology and secondary porosity as it was done in our previous work [1]. The objects under investigation are series of catalysts with different type of structure (mordenite, ZSM-5, natural clinoptilolite) and different developed mesoporosity which are important for increasing the kinetics of the reaction [2,3]. Various strategies to introduce mesoporosity: (i) treatment of microporous zeolites in an alkaline medium to create disordered secondary porosity and (ii) pillaring of zeolites with amorphous SiO_2 have been applied [4,5]. All samples have been characterized from point of view of surface area, pore volume and pore size by BET and BJH methods.

Finally, the amount of glycerol and heat effect of sorption have been obtained as specific values in respect to catalysts and glycerol molecules. As additional result of thermal analysis the preferable temperature for reactions of the glycerol conversion has been estimated. The obtained results are discussed with respect of catalytic efficiency of the studied modified zeolites in reactions of dehydration and carboxylation of glycerol.

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A CLASSICAL FORCEFIELD FOR SELENIUM OXYANIONS

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Selenium is one of the health-important natural occurring elements. Considered as an important micronutrient in low doses, it is becoming dangerous in higher doses [1]. Also, ^{79}Se radioactive isotopes are considered as a major dose-determining radionuclide which can affect the biosphere over geological timescale [2]. They are highly solvable in water and, therefore, highly mobile. There are many experimental studies on selenium oxyanions adsorption and solubility [3,4]. At same time, computational studies are limited, as there are no well-known classical forcefields developed for these molecules and mostly ab initio methods were previously applied to these molecules [5,6].

In this study we have developed a classical forcefield for SeO42–, SeO32–, HSeO3– oxyanions, comparable with the ClayFF potential [7]. This potential will allow to better study selenium mobility in aqueous solutions, as well as better understand its interaction with sorbents at the nano-scale.

The initial approximation for the force constants and charges were taken from double-hybrid DSD-PBEP86 density functional theory calculations with a SMD implicit solvent. The initial values were used in classical molecular dynamics calculations for further optimization, based on an algorithm described by Williams and Carbone [8]. The solvation energy estimation and Se-O bonds length were chosen to fit the force field parameters.

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STUDY OF THE STABILITY OF THE β-CYCLODEXTRIN/NAPROXEN INCLUSION COMPLEX IN A SUPERCRITICAL SOLVENT USING COMPUTER MODELING METHODS

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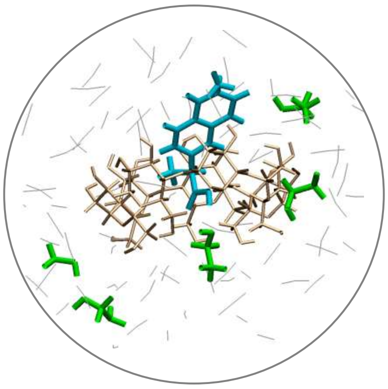
The research of the behavior of β-cyclodextrin/naproxen inclusion complex in supercritical (SC) carbon dioxide in the presence of a cosolvent has been carried out using the molecular dynamics method. The processes of encapsulation and release of naproxen and the role of the cosolvent in the formation and destruction of the inclusion complex have been studied. The influence of cosolvent concentration, temperature and density of the supercritical fluid on the probability of encapsulation of naproxen by cyclodextrin and on the duration of existence of the inclusion complex has been considered.



Naproxen, a widely used non-steroidal anti-inflammatory drug with analgesic and anti-inflammatory properties, was chosen as a model encapsulated substance. Complexation with cyclodextrins improves the rate and extent of its dissolution and increases the rate of absorption. Because the solubility of naproxen and cyclodextrins in pure SC CO_2 is low, encapsulation technology uses a cosolvent (ethanol) to increase it. We have studied the dynamic behavior of the β-cyclodextrin/naproxen complex in the SC solvent and establish to what extent the stability of the complex and the probability of its existence depend on the parameters of the state and the mole fraction of the ethanol. We have considered the influence of the factors on the encapsulation and release of naproxen, the structure of naproxen/β-cyclodextrin complexes, and the role of the cosolvent in the interactions between naproxen and β-cyclodextrin. Molecular docking, the DFT-B3LYP/6-31G method and the molecular dynamics method were used in the study.

The simulations showed that the β-cyclodextrin/naproxen inclusion complex does not exist permanently in the SC solvent. During the 500 ns observation period, episodes of naproxen encapsulation and release alternated. The duration of encapsulation episodes reached several tens of nanoseconds.

We found that the frequency of inclusion complex formation and the duration of its existence increase with increasing fluid density and ethanol concentration. The maximum total duration of encapsulation episodes was observed at T=313 K, ρ=0.84 g/cm^3 and 3.8 mol.% ethanol. It accounted for more than 52% of the total observation time.

The cosolvent molecules are localized in the solvation shell of the inclusion complex on the outside of the cyclodextrin body and within the boundaries of the rims. Ethanol forms HBs with both the host and guest molecules, thereby stabilizing the inclusion complex. Increasing ethanol concentration increases the probability of complex formation. If naproxen is outside the cyclodextrin cavity, ethanol occupies this cavity. When a naproxen molecule approaches the cyclodextrin from the fluid volume, it displaces ethanol from the cavity, and an inclusion complex is formed.

MODEL FOR MOLECULAR DYNAMICS SIMULATION OF LIGNIN DEPOLIMERIZATION AND SELF-ASSEMBLY IN WATER-ETHANOL MIXTURE

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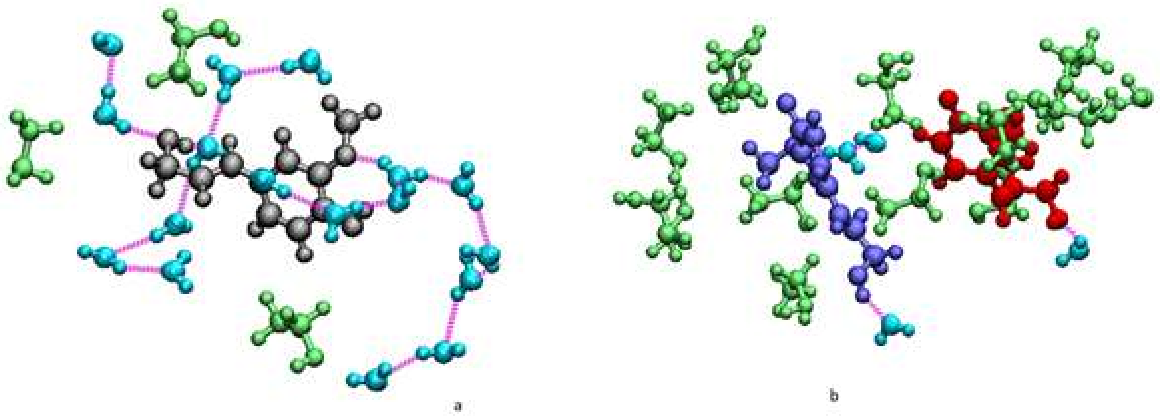
Lignin is a natural aromatic polymer that is of interest asa renewable resource for the synthesis of phenolic products widely used in organic synthesis,as well as for the production of new composite materials. The initial stage of lignin processing isits depolymerization. One of the promising directions of lignin depolymerizationis its treatment in organo-aqueous medium at elevated temperatures and pressures. As a result, the polymer molecule of lignin is destroyed, and its constituent monomers and oligomers pass into solution. It was found that subsequent treatment of solutions ofdepolymerized lignin at elevated temperatures leads to both further depolymerizationof lignin and repolymerization, accompanied by particle enlargement in solutions. Sinceconducting reactions under conditions of elevated temperature and pressure makes it difficultto obtain experimental data, in order to use lignin in practice to obtain informationat the molecular level about the structure of solutions formed during lignin depolymerization, the role ofsolution components in the processes of aggregation and depolymerization, on the solvation of lignols - the role of molecular dynamic modeling increases significantly.

The report presents the results of molecular dynamic modeling of the structure of water-ethanol lignin solutions at 573 K.Coniferylalcohol (CA) in the form of monomers and radical forms was chosen as the molecules of the model solute. The structureof the solutions is characterized usingradial distribution functions, and the lifetime of the water is estimated.-the native bonds between the molecules of water, ethanol andthe dissolved substance. It was found that ethanol stabilizesthe radical forms of molecules, and in the presence of radicalforms of coniferyl alcohol, the aggregation of its molecules proceedsmore efficiently.

A different nature of solvation was found for CA and its radicals. CA is predominantly solvated by water molecules, radicals by alcohol molecules. Two types of clusters have been detected: 1) CA molecules in a predominantly aqueous environment (Fig. a); 2) CA radicals mainly in an alcoholic environment (Fig. b). The cluster sizes correspond to the characteristic particle size found in aqueous ethanol solutions of lignin.



THEORETICAL MODELING OF THE HEAT CAPACITY IN CoV_2O_4 NEAR PHASE TRANSITIONS: A NEW APPROACH

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The CoV_2O_4 compound belongs to the class of spinels, widely used as catalysts, magnetic materials, matrices for doping with various 3*d* and 4*f* elements, etc. Spinels have a cubic structure with space group $Fd\overline{3}m$, many of them undergo phase transitions to ferro- and antiferromagnetic states.

In CoV_2O_4, two phase transitions take place from the cubic paraphase to the tetragonal phase with $I4_1/amd$ symmetry at a temperature T_{c1}= 142 K, then to the antiferromagnetic phase $I4_1/a$ at T_{c2}=59 K. The phase transitions are induced by irreducible representations of the Γ-point of the Brillouin zone with a star wave vector $\mathbf{k}_{11}$=0. The Gibbs free energy for describing phase transitions depends not only on temperature and pressure, but also on two single-component order parameters, one of which is completely symmetric. The expansion of free energy into a series in powers of order parameters has the form:

$$G = G_0(p,T) + a_1\eta + a_2\eta^2 + a_3\eta^4 + b_1\xi^2 + b_2\xi^4 + c_1\eta\xi^2 + c_2\eta^2\xi^2.$$

Here $G_0(p, T)$ is the equilibrium part of the Gibbs free energy, $a_1 = a_1'(T-T_1)$, $b_1 = b_1'(T-T_2)$, a_2, a_3 and b_2 are control parameters, and $a_3>0$, and $b_2> 0$ practically do not depend on external conditions and by renormalizing the coefficients can be taken equal to unity, the coefficients c_1 and c_2 do not depend on external conditions, but determine the topology of the phase diagrams. Model was built using methods of catastrophe theory (singularity theory) [1] and using equivariant vector fields [2]. The figure shows the theoretical temperature dependence of the heat capacity, calculated using the formula

$$c_p = -2T\left(a_1'\eta\frac{\partial\eta}{\partial T} + b_1'\xi\frac{\partial\xi}{\partial T}\right).$$

The inset shows the experimental dependence of the heat capacity from [3]. As can be seen from the figure, the experimental data satisfactorily correspond to the theoretical dependence of the heat capacity.

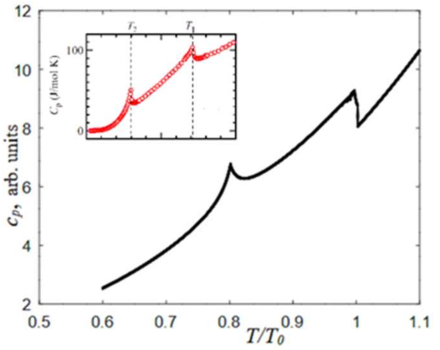

Figure. The theoretical temperature dependence of the heat capacity in CoV_2O_4. The inset shows the experimental dependence of the heat capacity [3].

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THERMOCHEMICAL PROPERTIES OF BULKY BENZOQUINONE-TYPE DERIVATIVES AT T = 298.15 K

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Quinones constitute a naturally occurring large class of aromatic compounds. They are found in several families of algae, fungi, bacteria, higher plants and arthropods.

Quinones are widely used for various applications, such as histological staining, rust prevention on metal surfaces, increasing the conversion efficiency of solar cells, using as sensors, pH indicators, pigments, inks and dyes for leather, wood, medicine, food and textiles. The perspective fields of the quinone-type compounds are the production of coloring substances as well as the regulation of free-radical processes (e.g., the control and inhibition of polymerization and photochemical reactions). In addition, quinone-type molecules are recognized among the scientific community in the field of coordination chemistry as one of the most widely used ligand platforms.

However, a considerable discrepancy between the number of reports in the fields of biochemistry, coordination chemistry, and applied chemistry for the quinone derivatives in contrast to their thermochemistry is observed. The investigation of bulky benzoquinone-type derivatives using a static-bomb combustion calorimeter with an isothermal cover allows us to reveal and analyze practically important patterns of changes in the thermochemical properties of compounds on their composition.

The present investigation is devoted to determine the combustion energies of the p-quinone and o-quinone derivatives and to calculate the standard thermochemical characteristics of their combustion and formation at T = 298.15 K. The samples of benzoquinones were ignited in an oxygen atmosphere (p = 30 atm) in the presence of paraffin. The investigated benzoquinones were added into the molten paraffin under the same conditions to prevent oxidation until ignition and to achieve complete combustion. The reaction between the chemically inert paraffin and the studied samples did not occur. After solidification, the samples were used in the calorimetric experiments. According to the obtained results, the completeness of the combustion process and the high purity of the studied benzoquinones were confirmed.

The obtained thermochemical characteristics of studied p-quinone and o-quinone derivatives were compared with similar literature data. It was established that, the enthalpies of formation of the compared 2,6-di-tert-butyl-*p*-benzoquinone, 3,5-di-tert-butyl-*o*-benzoquinone and 3,6-di-tert-butyl-*o*-benzoquinone, which are isomers, are the same within the experimental uncertainty. Inclusion of bulky tert-butyl groups in the benzoquinone molecule and a change in their mutual arrangement, as well as the introduction of various functional groups, leads to a decrease in the enthalpies of formation $\Delta_f H°$ of the compounds under study.

The research was carried out with financial support via State assignment in Research scientific laboratory of "Chemistry of natural products and their synthetic analogues" of Scientific Educational Centre "Technoplatform 2035", grant number FSWR-2024-0002.

SELF-CONSISTENT FIELD THEORY OF POLYELECTROLYTE SOLUTIONS IN CHARGED NANOPORES

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We investigate the mechanical and electrical properties of charged surfaces in polyelectrolyte solutions, utilizing a developed self-consistent field theory [1]. The grand thermodynamic potential of the model polyelectrolyte solution includes contributions of the electrostatic interactions in the mean-field approximation, the conformational contribution of flexible polymer chains, and the volume interactions described within the asymmetric lattice gas model framework. Profiles of the electrostatic potential and ion concentrations were obtained by solving the self-consistent field equations with specific boundary conditions.

An expression for the stress tensor was derived using a previously proposed approach based on the application of the second Noether's theorem. The total stress tensor incorporates standard contributions of isotropic hydrostatic stress and electrostatic (Maxwell) stress, along with the contribution associated with the conformational entropy of polymerized cations. By solving the self-consistent field equations for the one-dimensional case of a slit pore and applying the mechanical equilibrium condition, we obtained the dependence of the disjoining pressure on pore width.

We found that the disjoining pressure curves exhibit a noticeable non-monotonic behavior, attributed to polymer ejection from the pore volume, which also affects the profiles of differential electrical capacitance. Considering the presence of dielectric heterogeneity in such systems – the difference in dielectric permittivities of the polymer chain and the solvent – we analyzed how this factor influences the behavior of disjoining pressure and differential capacitance profiles.

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IN SILICO EXPLORATION OF DRUG-CANDIDATE CONFORMATIONAL SPACE IN SOLVATED ENVIRONMENTS: A COMBINED ATOMISTIC SIMULATION AND MACHINE LEARNING APPROACH

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Traditional experimental methods for drug and catalyst discovery are resource-intensive and time-consuming. The advent of high-performance computing has enabled the development of more efficient computational approaches. Density functional theory (DFT) is a widely used method, but its high computational cost limits large-scale molecule screening. To address this challenge, we propose the integration of machine learning (ML) techniques within Gradual Optimization Learning Framework (GOLF) [1]. This approach focuses on predicting key molecular properties such as conformation, ground state energy, and others using active learning algorithm. In practical applications, the behavior of molecules in solvent environments and their interactions with target proteins are a subject of major interest.

This work outlines the application of GOLF framework trained on forces and energies derived from ab initio calculations for efficient target molecule optimization within a solvent environment. Target molecules for optimization is selected from nablaDFT dataset [2].

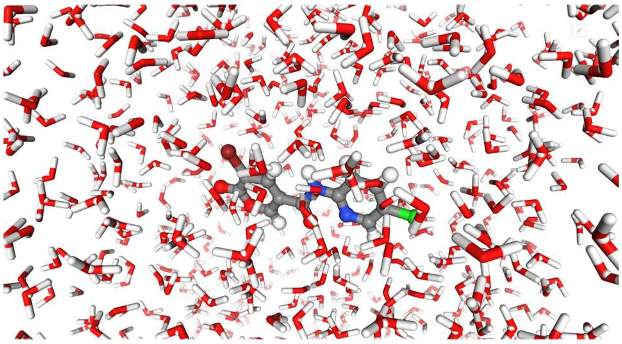

Figure 1. Snapshot of a drug-like molecule solvated in water.

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PAIRWISE ENTROPY AS A STRUCTURE PARAMETER FOR THE DESCRIPTION OF THE GLASS TRANSITION IN MOLECULAR SIMULATIONS

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In this work, we investigate the application of the pairwise entropy S_2 as a structural parameter for describing the glass transition in molecular and atomic systems in atomistic simulations. This is a parameter that can easily be computed from the partial radial distribution functions (RDFs) for polyatomic systems [1]. For molecular systems, we use the correction proposed by Nikitiuk et al. [2] to estimate the excess pairwise entropy relative to the ideal molecular gas. The temperature dependence of S_2 is analysed for a number of systems undergoing glass transition in molecular dynamics simulations, including Cu-Zr alloy (an atomic system), TIP4P water and SAFT-γ Mie model of toluene (rigid molecules) and multiple hydrocarbon models in the OPLS-AA potential (flexible molecules).

In all cases, the behaviour of the pair entropy with temperature is qualitatively similar. We find a "sickle"-shape pattern of the pairwise entropy dependence on the kinetic temperature. If we take S_2 as an approximation to the excess entropy of the system, the sickle-shape profile reflects a sharp drop of the heat capacity of the system below glass transition temperature. Those dependencies can be used to define a structural glass transition temperature by the maximum of the second derivative of $T(dS_2/dT)$. The results are similar compared to those obtained by the calorimetric criterion, as opposed to the glass transition temperatures obtained from another RDF-based characteristic, second-peak splitting [3, 4]. Another feature is that the glasses obtained at lower cooling rates always have lower pairwise entropy, so that it is a characteristic of the relaxation degree. That means, it has potential use to study glass aging and rejuvenalization under cyclic mechanical loading. For some substances we find that the changes in the pairwise entropy are more prominent than the changes in the total heat capacity or enthalpy, so that the proposed structural parameter may lead to a more convenient way to determine the glass transition temperature in molecular simulations.

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NOVEL GLYCOSYLATED CATIONIC PORPHYRINS: OPTICAL PROPERTIES, PROTONATION EQUILIBRIA, SINGLET OXYGEN GENERATION

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Tetrapyrrolic macrocycles are widely use as photosensitizers (PS) in photodynamic therapy (PDT) and photodynamic diagnosis. The one of the key problems of developing the ideal PS should be solved is high selectivity to accumulation in target tissue. Promising strategy for target drug delivery is adding to PS molecules saccharide residues. Insertion into the cationic porphyrin macrocycle, which is characterized by high-solubility and photodynamic activity of bulky saccharide moieties, capable of interacting with specific receptors on the cell membrane surface may decrease the undesirable aggregation tendency and provide rapid and selective accumulation of PS in tumor tissues and increase diagnostic and therapeutic efficacy. A further feature of glycosylated porphyrin derivatives is the chirality of carbohydrate moieties provides ability to stereochemical molecular recognition. Here we present the investigation of chemical and photophysical properties of cationic glycosylated porphyrin derivatives based on 5,10,15,20-tetra(*N*-methylpyridine-3-yl)-porphine $\mathbf{H_2P}(3'\text{-MePy}^+)_4$ with (β-D-galactopyranosyloxy)phenyl meso-substituents: 5-(4-(β-D-galactopyranosyloxy)phenyl)-10,15,20-tris(N-methylpyridine-3'-yl)porphine $\mathbf{H_2P}(3'\text{-MePy}^+)_3(\text{PhG})$ and 5,15-bis(4-(β-D-galactopyranosyloxy)phenyl)-10,20-bis(N-methylpyridine-3'-yl)porphine $\mathbf{H_2P}(3'\text{- MePy}^+)_2(\text{PhG})_2$ as a potential model of photosensitizers for PDT [1]. An increase in the fluorescence quantum yield was found with an increase in the number of saccharide fragments in macrocycle. Comparative method based on monitoring the pyridoxine photodegradation in phosphate buffer solution under red light irradiation has been established that the observed rate of pyridoxine decomposition is higher in the presence of $\mathbf{H_2P}(3'\text{-MePy}^+)_3(\text{PhG})$ and $\mathbf{H_2P}(3'\text{-MePy}^+)_2(\text{PhG})_2$ as compared with $\mathbf{H_2P}(3'\text{-MePy}^+)_4$, which indicates a higher efficiency of singlet oxygen generation by glycosylated photosensitizers. It was found that values of stepwise protonation constants of the porphyrin $\mathbf{H_2P}$ platform of obtained photosensitizers are close, and protonation accompanied by a significant increase in the intensity of long-wave absorption, fluorescence intensity and fluorescence quantum yield. It was shown that the insertion of saccharide fragments shifts the equilibrium of $\mathbf{H_2P}$ protonation towards physiological pH values which is the starting point for pH-activation of porphyrin photosensitizers fluorescence in more acidic tumor tissue.

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THE EFFECT OF AN EXTERNAL HOMOGENEOUS MAGNETIC FIELD ON THE SYNTHESIS OF FE_2O_3 NANOPARTICLES IN A PULSED UNDERWATER DISCHARGE PLASMA

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Magnetic particles are currently widely used in the creation of nanocomposite catalysts, data storage systems, as contrast agent in magnetic tomography, for microfluidics tasks etc. Iron oxides are a promising material due to their wide distribution, stability, and biocompatibility. The most widely used form is Fe_2O_3, which has four crystalline polymorphic modifications. Among these, the most extensively studied are α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite), β-Fe_2O_3 и ε-Fe_2O_3. All the mentioned oxides have various crystal structures and possess different types of magnetism.

Iron(III) oxide nanoparticles were synthesized through plasma pulsed underwater discharge. The experimental setup consisted of a 100 ml glass cell with two electrodes, a temperature sensor, and a cooling jacket. The cell was placed in an adjustable interpole gap (80 mm) of an electromagnet, with the induction of a uniform magnetic field varying between 0-1000 mTl. The iron electrodes in the cell were arranged parallel and perpendicular to the magnetic field lines.

The oxide samples obtained from the plasma discharge were analyzed using X-ray phase analysis, IR, Raman spectroscopy, and electron microscopy. The study found that the presence of a magnetic field in an underwater pulse discharge significantly affects the discharge characteristics. The magnetic field restrains the discharge, resulting in decreased amplitude values of current and voltage, as well as a lower frequency of discharge pulses. Furthermore, the presence of a magnetic field accelerates the agglomeration and growth of iron oxide nanoparticles, leading to the formation of larger particles. The crystal structure of plasma process products is also affected by the position of magnetic field force lines in relation to the plasma discharge. Depending on this position, Fe_2O_3 can form α-, γ-, and ε-structures.

This work was supported by a grant from the Russian Science Foundation, project №23-23-00276.

PHOTOSENSITIZER BASED ON BICHROMOPHORIC α,α-bis(BODIPY): SPECTRAL PROPERTIES, SINGLET OXYGEN GENERATION

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BODIPY dyes are versatile molecules for designing new photosensitizers (PS), fluorescent theranostics for photodynamic therapy (PDT) and antimicrobial photodynamic therapy (APDT). Oligomerization is a new method to create BODIPY PSs without heavy halogen atoms, which seem more attractive as PSs. The main factors for determining the spectral and generation characteristics of BODIPY bichromophores are the attachment positions of the monomeric domains and the nature of the pacer that binds them The results of a study of the features of their structure, photophysical characteristics and solvatochromic effect of a new α,α-bis(BODIPY) bichromophore are presented in this work. The values of extinction coefficients are high ($\lg\varepsilon$ is 4.78÷4.83) which indicates its high light-absorbing ability and long-wavelength absorption band exciton splitting ($\Delta\nu_{ES}$) is 2595 – 2665 cm^{-1} of the depending on the solvent (Figure 1).

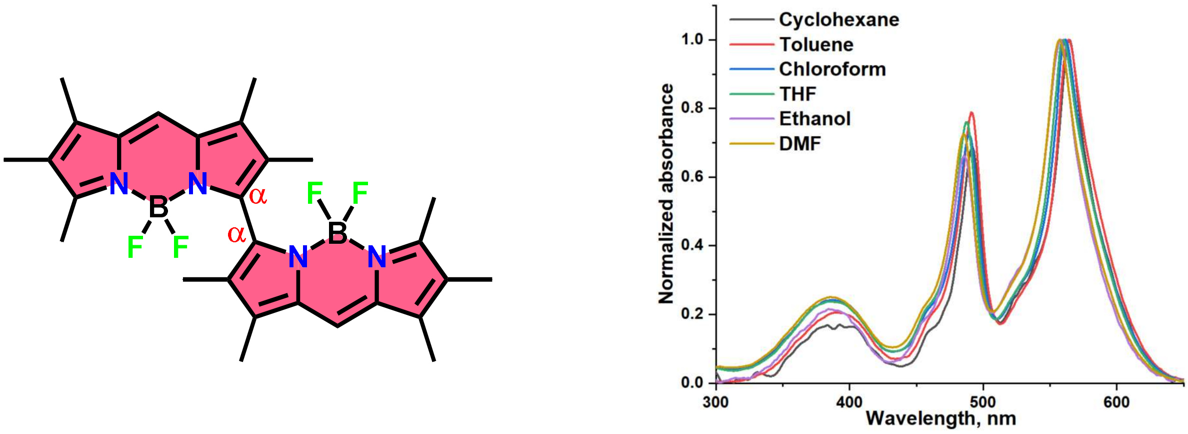

Figure 1. Object of study α,α-bis(BODIPY) and normalized absorption spectra in organic solvents

The fluorescence quantum yield (Φ_{fl}) and the quantum yield of singlet oxygen generation (Φ_Δ) are highly sensitive to the solvent nature. The fluorescence efficiency is relatively high in non-polar inert solvents (Φ_{fl} = 55%). Singlet oxygen generation efficiently in the intermediate polarity THF (Φ_Δ = 87%) and greatly decreases till 2 – 10% in polar (acetonitrile, DMF, ethanol). α,α-bis(BODIPY) demonstrated the dual functionality of a promising theranostic.

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CORRESPONDENCE PARTICIPATION

SELF-ORGANISATION OF COMPLEX CHEMICAL SYSTEMS. OXIDATION OF HYDROCARBONS IN MICROHETEROGENEOUS SYSTEMS BY ADDITIVES OF SURFACTANTS

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Regularities of oxidation of hydrocarbons (dodecane, ethylbenzene, cumene, limonene) (RH) and decomposition of hydrocarbons in microheterogeneous systems formed by additions of surfactants and solid microdispersed systems in hydrocarbon medium have been investigated [1,2].

At the same time, many, many real systems are microheterogeneous, water-organic or become so in the process of exploitation Additions of surface active substances (surfactants) in hydrocarbons regulate the microstructure of the medium, prevent the release of water dissolved and formed in the process of oxidation.

A pronounced influence of the surfactant nature on the transformation mechanism has been established. Ionogenic micelle-forming surfactants including a linear hydrocarbon fragment catalytically accelerate the decomposition of ROOH, whereas non-ionogenic surfactants soluble in RH and solid oxides practically do not affect the reaction rate. A detailed study of the kinetic patterns of decomposition in the presence of anionic alkyl sulfates and cationic DTAB showed that the accelerating effect of surfactants is associated with their colloidal properties, namely, with the formation of joint aggregates such as inverted micelles, in which the decomposition of the peroxide bond is facilitated.

Synergism of the inhibitory action of sodium alkyl sulfate mixtures with phenolic antioxidants in the oxidation of various hydrocarbons has been established for the first time. At oxidation of ethylbenzene with small additives (<1%) of sodium dodecyl sulfate (SDS) a unique case of effective self-inhibition was established, the mechanism of which includes two positions: hydroperoxide - the main source of free radicals is heterolytically decomposed in microaggregates jointly with SDS, the decomposition occurs selectively with formation of acetaldehyde and phenol. Comparison of the results of kinetic studies, analysis of products during oxidation with surfactant additives revealed a number of chemical analogies in the action of surfactant microaggregates and acidic zeolite and superacid catalysts, namely: olefin formation during oxidation of dodecane and isopropylbenzene, structural specificity during ROOH decomposition, isomerisation and dehydrogenation of limonene in inert atmosphere; similar influence of water on catalytic activity - promotion by microquantities and deactivation at full filling of the active surface; close dimensional characteristics.

Based on the results obtained, a hypothesis of similar structure of the catalytic microreactor of RH and ROOH transformation in reversed micelles-microemulsions of ionogenic surfactants and in micropores of zeolites was put forward.

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EFFECT OF EXTREME HIGH FREQUENCY ELECTROMAGNETIC FIELD AND HYDROTHERMAL PROCESSING CONDITIONS ON THE SYNTHESIS OF NANO-SIZED FERRIT CATALYSTS FOR THE PETROCHEMICAL FIELD

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Ferrites are widely used in radio engineering, radio electronics, computing, etc. This is connected with their ability to create magnetism with semiconductors and dielectrics. Ferrites are also used in the production of polyfunctional heterogeneous catalysts in petrochemical processes. Oxides, hydroxides, oxalate and carbonates (sometimes they are co-precipitated in solution) or their salts (nitrates, sulfates, double sulfates) are used as primary components for obtaining these substances. For soluble ferrites, hydrothermal processing of sodium carbonate or hydroxide, as well as ammonium chloride solutions is used. The known synthesis methods of metal ferrites are as follows: high-temperature hydrothermal processing and also cooking of suitable components, which consumes a lot of energy. In order to increase the rate of interaction of solid phases at the last stage of ferrite formation, recently, in addition to the thermal method, work has been carried out with mechanical, ultrasonic influence on the reaction mixture or with the influence of various other physical means [1]. The heat transfer properties of the synthesized ferrite samples are characterized by the ability to absorb microwaves at a fairly high level. The heat transfer properties of the synthesized ferrite samples are characterized by their ability to absorb microwaves at a fairly high level. Obtaining ferrites in the extremehigh frequency (EHF) electromagnetic field is more promising in terms of energy and time [2]. For this purpose, a nano-sized $CoFe_2O_4$-ferrite catalyst has been synthesized as a metal oxide catalyst, which has a wide application field in oxidation-reduction processes in the field of petroleum chemistry. Thermal treatment of ferrite samples for synthesis was carried out in a microwave oven EM-G5593V (Panasonic) with a 25-liter resonator, a magnetron with a power of 200–800 W, operating at a frequency of 2450 MHz. The temperature of the reaction zone was measured by means of CEM DT-8858 infrared pyrometer, varying in the range of $50\text{-}1300^0$C.To obtain $CoFe_2O_4$-containing ferrite, nitrate salts of the elements Fe and Co $[Fe\ (NO_3)_3 \cdot 9H_2O,\ Co(NO_3)_2 \cdot 6H_2O]$ were precipitated with ammonium hydroxide -(NH_4OH) using the co-precipitation method. The influence of hydrothermal treatment conditions on the resulting hydrogel after washing Fe- and Co-hydroxides was studied. The absorption dynamics of the hydrogel was studied under conditions of microwave synthesis and after hydrothermal treatment with EHF rays.The process was checked at different times and temperatures. For this purpose, by hydrothermal treatment of the hydrogel under certain optimal conditions – for 3 hours at a temperature of 250°C, drying at 100–115 ^{0}C under the influence of EHF (extremely high frequency) at a power of 160 W for 3–5 minutes and incandesce at temperatures of 400–450 and 500–550°C at a power of 800 W for 5 minutes, a nano-sized ferrite catalyst $CoFe_2O_4$ was obtained.The phase composition was studied by means of RFA. Obtaining 100% $CoFe_2O_4$ both at annealing temperatures of 500-550°C and 400—450°C is beneficial both from the point of view of energy saving and from the point of view of a positive result.As a result, with considerable saving of energy and time, it was possible to obtain nano-sized ferrite catalyst by annealing at a temperature of 400–450°C with the effect of hydrothermal processing and EHF waves.

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ENCAPSULATION OF PHASE CHANGE MATERIALS IN HIGHLY POROUS POLYMERS

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Latent heat storage using phase change materials (PCM) is considered to be one of the most effective and attractive methods of thermal energy storage. Most of these materials have low thermal conductivity and a tendency to spread, which often limits their applications. Therefore, research into novel composites and additives to form thermally stable and efficient PCM with improved heat transfer is of interest to promote and implement more sustainable practices in the construction industry [1]. Encapsulation of PCM in highly porous polymers is a promising approach to the manufacture of such materials. A highly porous polymeric material can be produced by polymerizing high concentration W/O emulsions containing a monomer or mixture of monomers as the organic phase. After polymerization and removal of the aqueous phase, a porous structure similar in structure to the initial emulsion is formed [2, 3].

In this work, polymeric PCM based on beeswax and paraffin wax were produced. A highly porous polymers were prepared by polymerizing a dispersion medium of a highly concentrated W/O emulsions consisting of styrene and divinylbenzene. Sorbitan monooleate (Span 80), was used to stabilize the emulsions. Ammonium peroxodisulfate was used to initiate polymerization of the organic phase of the emulsions. The fraction of the aqueous phase in emulsions was 90 vol.%.

The average pore size in the prepared polymer materials was 3.4 μm. Differential scanning calorimetry (DSC) was used to determine the melting points of beeswax and paraffin wax in the pores of the copolymer. The melting point of paraffin wax was found to be 51 °C. The melting point of beeswax was 62 °C. Microencapsulation of waxes in the pores of polymeric materials resulted in the melting point of paraffin being reduced to 45.8 and that of beeswax to 59.7.

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THERMODYNAMICS OF NITRIDE EVAPORATION

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The availability of reliable data on the thermodynamics of evaporation of chemical compounds that are part of the processed raw materials or initial for the synthesis of materials with required properties, including nanostructured, is essential for the development of the physicochemical basis of pyrometallurgical processes. Including processes under the influence of highly concentrated energy sources on the substance, especially processes of plasma chemistry and plasma metallurgy, for which vaporisation is a determining factor for the results of the technological process.

The thermodynamic analysis of the nitride evaporation processes we have shown that all elements of the Mendeleev table form chemical compounds with nitrogen in both condensed and vapour (gas) states [1-4]. It was found that the molecular composition of the vapour-gas phase of many chemical compounds and their mixtures is significantly more complex and diverse than previously imagined. In addition to monomeric molecules in the vapours of nitrides were found a variety of gaseous molecules of these compounds.

Experimental results on the thermodynamics of evaporation and dissociation of nitrides of almost all elements of the periodic system of D.I. Mendeleev published in the world literature up to 2020 are systematised for the first time. A wide range of data on vapour pressure, vapour composition, as well as thermodynamic properties of gaseous nitrides obtained from the study of evaporation processes are presented. Temperature dependences of vapour pressure over MeN systems are obtained. Tables on enthalpies of atomisation and formation of gaseous nitrides and vapour composition over nitrides of chemical elements located by groups of the periodic system are given.

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THERMODYNAMICS OF MICELLIZATION IN AQUEOUS SYSTEMS OF SURFACTANTS IN THE PRESENCE OF BIOLOGICALLY ACTIVE COMPOUNDS

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Micellization is one of the important processes of the aqueous solutions of surfactants, because due to micellization the new aggregates (micelles, bimicelles, vesiculas) are formed which changes the properties of system and type of intermolecular interactions. Due to the study of micellization thermodynamics it is possible to reveal the effect of different factors and interactions, which, in its turn, get possibility to control the micellization process having huge importance for processes of polymerization, emulsion stabilization, for evaluation of basic phenomena of enzymatic, biochemical and membrane processes in biological systems, in pharmacology and food industry and so on.

The effect of amino acids (glycine, alanine, phenylalanine, serine, leucine, lysine, aspartic acid) and vitamins (vitamin C and nicotinic acid) on the micellization of anionic, cationic and nonionic surfactants has been studied. From the determined data of thermodynamic parameters for studied systems it is followed that the values of Gibbs free energy of micellization ΔG_M^0 becomes more negative with the increase of temperature which is due to increasing hydrophobic effect in high temperatures. At the same time the values of ΔG_M^0 become less negative with the increase of amino acids and vitamins concentration in aqueous systems of ionic surfactants. It means that with increase of amino acids and vitamins concentration the micellization becomes less favorable in aqueous systems of ionic surfactants. Another behavior is in aqueous systems of nonionic surfactants- the values of ΔG_M^0 become more negative with the increase of amino acids and vitamins concentration; the increase of amino acids and vitamins concentration favors the micellization in the aqueous systems of nonionic surfactants. The negative values of enthalpy of micellization ΔH_M^0 indicate the strong interactions between amino acids/vitamins and micelles. The behavior of ΔH_M^0 in the studied systems lets us to conclude that at the higher concentrations of nicotinic acid, phenylalanine, lysine and at the lower concentrations of glycine, alanine, serine, leucine, aspartic acid and vitamin C the strongest interactions exit between micelles and amino acids/vitamins which are due to localization of amino acid/vitamin on the outer palisade layer of micelle (Figure). The values ΔS_M^0 are negative for studied systems and decrease with the increase of amino acids and vitamins concentration. The positive values of ΔS_M^0 indicates that for studied systems in micellization process the entropy is dominant. The detected observation is due to reorganization of water molecules at the interactions of amino acid/vitamin with micelle.

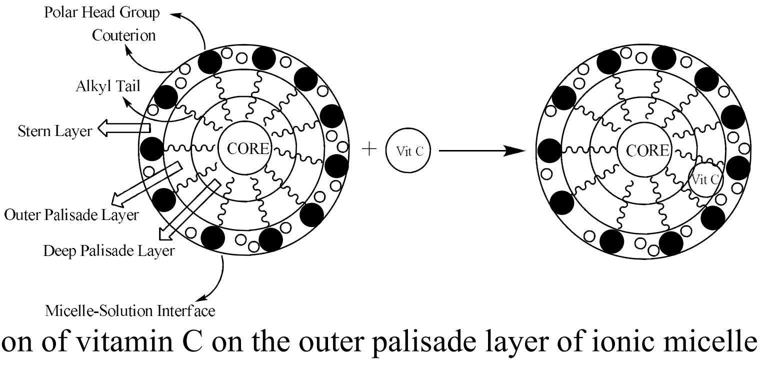

Figure. Localization of vitamin C on the outer palisade layer of ionic micelle.

CALORIMETRIC DETERMINATION OF THE ENTHALPY OF FORMATION OF SILVER(I) MONOCOMPLEX WITH 1-METHYL-2-MERCAPTIOIMIDAZOLE

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The study of the reactivity of heterocyclic thioamides exhibiting antithyroid activity is of scientific and practical interest. Research in the field of thermodynamics of complex formation of metal ions with imidazoline(imidazolidine)-2-thiones and their derivatives contributes to the development of coordination chemistry of thio compounds. Thermodynamic parameters of complexation can be determined by various complementary methods, which increases the reliability of the results obtained.

The heat effects of complexation reactions can be found experimentally by direct calorimetric measurements and derived from equilibrium constants obtained at different temperatures (temperature coefficient method). This work presents the results of a calorimetric study of the reaction of the formation of a mono-complex of silver(I) with 1-methyl-2-mercaptoimidazole in water at T = 298.15 K. The results are compared with the results obtained previously potentiometrically [1] using the temperature coefficient method. Thermochemical experiments were performed on a TAM III isothermal calorimeter with a titration module equipped with a 20 ml reaction cell. In calorimetric experiments, the initial concentration of $AgNO_3$ in the cell was $1.0 \cdot 10^{-4}$ mol/l, and the concentration of the titrant (1-methyl-2-mercaptoimidazole) was $1.36 \cdot 10^{-2}$ mol/l. It was established the formation of only a mono-complex of silver (I) with 1-methyl-2-mercaptoimidazole under these experimental concentration conditions. It was established in [1] that silver(I) reacts with 1-methyl-2-mercaptoimidazole in a stepwise to form three complex particles, the stability of which decreases with increasing temperature. Mathematical processing of the results of calorimetric experiments was carried out using the TAM Assistant program and using the stability constant value of the silver(I) monocomplex with 1-methyl-2-mercaptoimidazole ($\lg K$ = 6.34±0.02) obtained in [1]. The thermodynamic parameters of complex formation were obtained as: $\Delta H = -63.9 \pm 4.7$ kJ/mol; $\Delta G = -36.18$ kJ/mol; $\Delta S = -93.04$ J/(mol K). Processing the results of calorimetric titrations using the TAM Assistant program for the purpose of jointly determining the stability constant and enthalpy of complexation allowed us to obtain the following parameters: $\lg K = 4.8$, $\Delta H = -79$ kJ/mol, which reflect the maximal mutual correlation between the stability constant and enthalpy of complexation. Although the heat effect of the reaction should not depend on the determination method, values obtained from the temperature coefficient of equilibrium constants ($\Delta H = -60.1$ kJ/mol; $\Delta G = -35.5$ kJ/mol; $\Delta S = -82.61$ J/(mol K) [1]) differ somewhat from the results obtained calorimetrically, but do not contradict the latter, which allows us to conclude that they are in satisfactory agreement each other.

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THERMODYNAMIC MODEL OF THE STRUCTURE OF SODIUM BORATE GLASS AND THE TEMPERATURE DEPENDENCE OF ITS DENSITY

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The temperature dependence of the density of sodium borate glass $20Na_2O{\cdot}80B_2O_3$ (mol %) stabilized below its glass transition point $T_g = 450°C$ reported in [1] is analyzed using the approach based on the thermodynamic model of associated solutions [2,3]. Glasses are considered as solutions formed from chemical groupings whose stoichiometry and structure are similar to those of crystalline compounds that form in a given system. Using the formalism of this model, the equilibrium concentrations of various groupings present in the given glass, which determine its chemical structure, are calculated. If the glass is stabilized at 450–390°C, its density increases with decreasing stabilization temperature and becomes constant at 402°C (Figure). The chemical structure of $20Na_2O{\cdot}80B_2O_3$ glass (melt) calculated at 1200–400°C [2] reveals that, with decreasing temperature, the content of the dominating chemical grouping $Na_2O{\cdot}4B_2O_3$ increases up to 93% at the expense of the groupings $Na_2O{\cdot}2B_2O_3$ and B_2O_3 whose fractions become minimal at 402°C (Table). Since the chemical grouping $Na_2O{\cdot}4B_2O_3$ brings into glasses tetraborate superstructural unit [3], which is characteristic of the corresponding crystalline compound, it can be assumed that, at 402°C, the glass structure becomes as similar to that of the corresponding crystal $Na_2O{\cdot}4B_2O_3$ as is possible under the chosen experimental conditions. This assumption is confirmed by the fact that, at this temperature, the density of stabilized glass reaches the largest value.

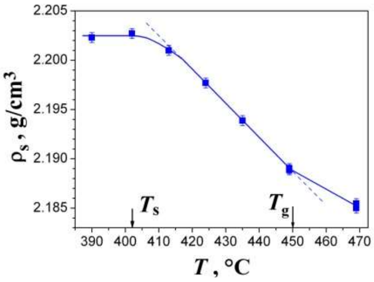

Figure. Density, ρ_s, of the stabilized $20Na_2O{\cdot}80B_2O_3$ glass as a function of the stabilization temperature [1]. The density was determined after the glass sample was cooled to room temperature. The density below T_g first increases with decreasing temperature and then reaches a constant value at temperature T_s.

Table. The chemical structure of the composition $20Na_2O{\cdot}80\ B_2O_3$ as a (meta)stable melt and glass after its stabilization at T_g and below it.

Chemical groupings	Mole fractions of the chemical groupings in the composition $20Na_2O{\cdot}80\ B_2O_3$ at different temperatures				
	Stable melt	Metastable melt		Stabilized glass	
	1200°C	800°C	600°C	450°C (T_g)	402°C (T_s)
$Na_2O{\cdot}4B_2O_3$	0.35	0.68	0.81	0.90	0.93
$Na_2O{\cdot}2B_2O_3$	0.17	0.13	0.09	0.07	0.06
$Na_2O{\cdot}B_2O_3$	0.04	0.01	0	0	0
B_2O_3	0.44	0.18	0.10	0.03	0.01

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ON THERMALLY INDUCED STRUCTURAL TRANSFORMATIONS IN THE TERNARY NiCuFe NANOALLOY

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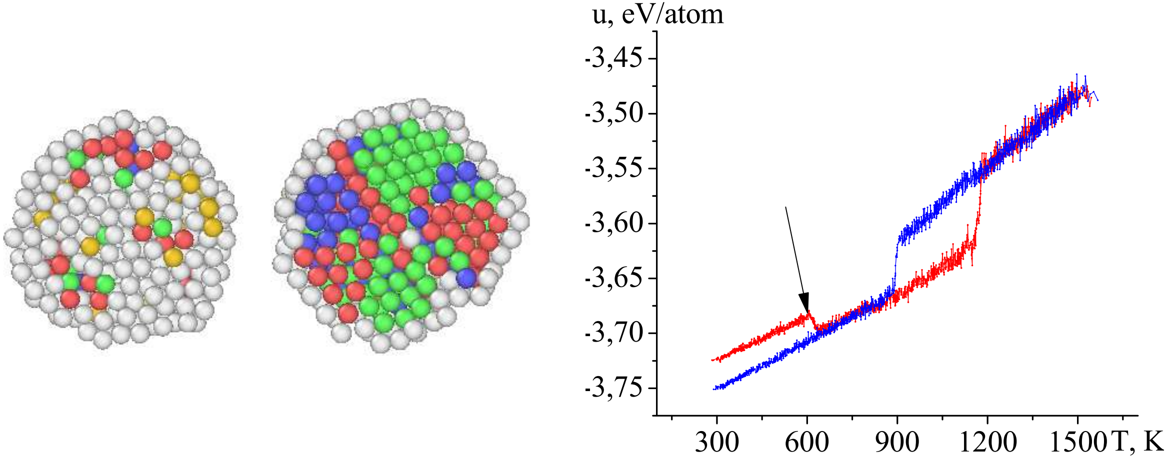
Currently, the investigation of structural transformations (crystal-amorphous state) in multicomponent nanoparticles is of interest from the point of view of practical applications, including in the temperature range significantly below the melting temperature [1]. Using the molecular dynamics method in software [2], the possibility of transition from an amorphous structure to a crystalline one in the ternary $Cu_{300}Fe_{300}Ni_{300}$ equiatomic nanoalloy during heating process was investigated. The embedded atom model was used as an interatomic potential [3]. Structural transition was determined using the software [4]. A nanoparticle (NP) with an amorphous structure (Figure 1a) was obtained in the first heating-cooling cycle (heating and cooling rates are 1 K/ps respectively). In larger NPs (that investigated in this work) the crystalline structure is fixed at the end of the first cycle. The transition of NP to the crystalline state upon heating (Figure 1b) was recorded in the second «heating-cooling» cycle (temperature rate 0,1 K/ps) at approximately 610 K (Figure 1c). The crystallization process, including the formation of amorphous NPs, is determined by temperature, its rate of change, and NP size.



a b c

Figure 1. The transition from an amorphous state to a crystalline state upon heating the ternary $Cu_{300}Fe_{300}Ni_{300}$ NP: (a) amorphous phase at 600 K (green – fcc structure, red – hcp structure, blue – bcc structure, yellow – icosahedral structure, gray – unrecognized structures); (b) crystalline phase at 630 K; (c) caloric dependence of specific potential energy (heating – red curve, cooling – blue curve).

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STRUCTURAL TRANSFORMATIONS IN BIMETALLIC Ni-Ag NANOPARTICLES WITH JANUS STRUCTURE

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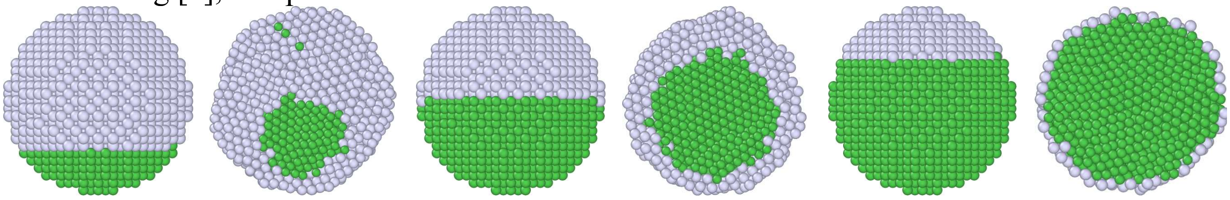
Trends in structural transformations and a certain stable structure for binary nanoparticles are largely determined by the composition of the components [1]. Even for binary nanoparticles, there is variability in the types of structure (core-shell, Janus structure, uniform distribution of components) [2]. In order for all the specific manifestations in the behavior of binary metal nanoparticles to be identified, an integrated approach is used that combines alternative methods of atomistic modeling: the molecular dynamics method and the Monte Carlo method [3]. To study the local structure, as a rule, software [4] is used.

In this work, bimetallic Ni-Ag nanoparticles with an initial Janus structure are used as research objects. It has been shown that during thermal exposure the formation of a core-shell structure is always observed. Even in nanoparticles enriched with nickel atoms, a monolayer of silver is formed on the surface of the nanoparticle. It is also of interest to analyze the caloric dependence of the specific potential energy for such Janus structures. The curves corresponding to melting and crystallization can have a stepped appearance, and this appearance is caused simultaneously by a strong structural rearrangement of atoms due to the special spatial arrangement of the components and directly by the processes of melting and crystallization. However, the degradation features of the Janus structure in bimetallic nanoparticles are of practical interest, because the technological process of forming Janus structures can be considered one of the simplest compared to the other structures noted above. Moreover, with rapid heating of such nanoparticles, for example, in the process of selective laser melting [5], it is possible to obtain a core-shell structure.



Ag3325-Ni675 Ni2000-Ag2000 Ni675-Ag3325

Figure 1. Initial and final configurations (nickel atoms - green, silver atoms - gray) obtained during the cooling process: Monte Carlo method.

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KINETIC AND THERMODYNAMIC PARAMETERS OF LA(III) IONS SORPTION ON SILICA GEL MODIFIED WITH MONOETHANOLAMINE

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Kinetic and thermodynamic characteristics of the La(III) ions sorption from nitrate media at pH 6.8–7.2 on ASK silica gel modified with monoethanolamine (ASK-EA) were determined. In this range of pH values the maximum of La^{3+} ions recovery (95–98%) without formation of hydroxide precipitates was observed. Dependences of lanthanum (III) ions sorption as a function of time and equilibrium adsorbate concentration were obtained at 296, 303 and 313 K.

The kinetic curves were processed using equations for pseudo-first (Lagergren) and pseudo-second (Ho and Mackay) orders [1]. The time dependences of the ASK-EA sorption capacity are better described by the model for pseudo-second order ($r^2 \approx 0.999$), i.e. the extraction process is both affected by the adsorbate concentration and the number of active centres on the adsorbent surface. The adsorption rate constant decreases significantly ($k_{296} = 141.27$, $k_{303} = 27.46$, $k_{313} = 24.01$ g·mmol^{-1}·min^{-1}) with the temperature increases, suggesting that the recovery is due to physical adsorption.

The sorption isotherms of La(III) ions at different temperatures were processed in the coordinates of the equations of Langmuir (model of monomolecular adsorption), Freundlich (model of sorption on a heterogeneous surface), Dubinin-Radushkevich (extended Langmuir model) and Temkin (considers the effects of indirect adsorbate–adsorbate interaction on the adsorption process) [2]. The experimental data are most accurately described by the Temkin model. During the adsorption process there is a gradual and regular filling of active centres with the formation of strong intermolecular contacts [3]. The adsorption constant decreases ($K_{296} = 9191446$, $K_{303} = 2566528$, $K_{313} = 1759484$) with increasing temperature, which means that the equilibrium shifts towards desorption. The thermodynamic parameters of the process were established: Gibbs energy ($\Delta G \approx -38$ kJ/mol), integral heat of adsorption ($\Delta H \approx -72$ kJ/mol) and entropy ($\Delta S \approx -111$ J/mol·K) have negative values, i.e. the extraction process proceeds spontaneously, has exothermic character, and adsorption prevails over the desorption process.

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CALCULATION OF CO_2 AND CH_4 ISOBARS USING THE FRACTAL STATE EQUATION

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Based on the previously proposed method [1], the equation of state for carbon dioxide CO_2 and methane CH_4 were calculated. The following expression was used for calculation:

$$P = \rho RT \left\{ 1 + \rho B + (1-\alpha)\left[\ln\left(\frac{eM}{\rho N_A} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right) + \psi(1) - \psi(2-\alpha) - \rho B \right] \right\}.$$

The proposed model implies that fitting parameter *α* depends both on density of substance, and its temperature. However, in [2] it is shown, that for CO_2, there is no temperature dependence. For CH_4, it is discovered, that temperature dependence is not significant and weakens approaching to 1000 K. This allows, for the given substances, to approximate the dependence of *α* on density by a polynomial and then use it in calculations at any temperature. Then, it is possible to calculate a set of isotherms with a small temperature step, and transit to isobar selecting on each isotherm a point with the required pressure. The figures 1 and 2 present the calculation result of CO_2 and CH_4 isobars for pressures 2, 5, 10 and 20 MPa. Symbols indicate experimental data from [3, 4, 5], curves show the calculations. As the figures show, the calculation results are in good agreement with the experimental data. For CH_4 weak temperature dependence of *α* leads to a small deviation is calculations at a low temperature and high pressure.

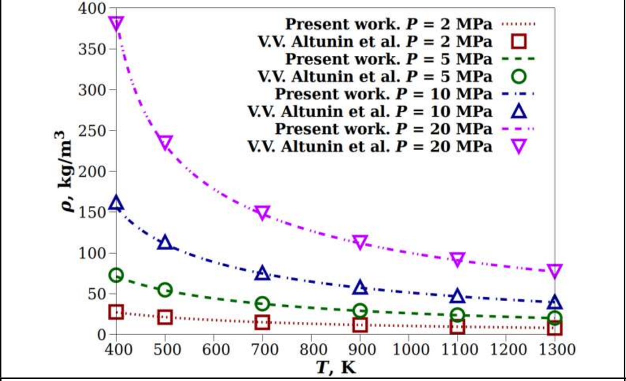

Figure 1. CO_2 isobars for various pressures. Symbols show experimental values, curves – Fractal equation of state calculation.

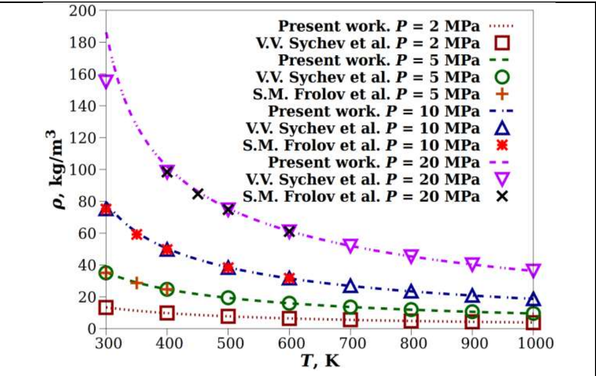

Figure 2. CH_4 isobars for various pressures. Symbols show experimental values, curves – Fractal equation of state calculation.

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INVESTIGATION OF EQUILIBRIUM PROPERTIES OF HEXANE AND ITS ISOMERS BY ACOUSTIC METHOD

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Hexane and its isomers 2-methylpentane and 3-methylpentane can be referred to substances with similar intermolecular forces but different particle configurations. Liquid 2-methylpentane and 3-methylpentane (Sigma-Aldrich, mole fraction 99%) were used after purity control by refractive index and density value without further purification. The ultrasonic wave velocity in the liquids was determined by the pulse-phase method of one fixed distance at frequencies of 1 and 3.3 MHz. No ultrasonic velocity dispersion was found in the specified range. The density was measured at atmospheric pressure by the pycnometric method with an error not exceeding ±0.1%. Measurement of ultrasonic wave velocity at elevated pressures was carried out by the acoustic piezometer method. In the article on the basis of experimental data obtained by the authors on the saturation line for hexane and its isomers 2-methylpentane and 3-methylpentane the possibility of predicting their density in the single-phase region on the basis of fluctuation theory is considered.

HIGH-TEMPERATURE HEAT CAPACITY OF THE $Ca_3Sc_{2-x}Y_xGe_3O_{12}$ SOLID SOLUTIONS

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Garnet-structured compounds ($A_3B_2C_3O_{12}$) are promising ionic conductors and microwave dielectrics, matrices for phosphors. For example, $Ca_3Sc_2Ge_3O_{12}$ and $Ca_3Y_2Ge_3O_{12}$ are one of the most important families of hosts for luminescent dopants, especially for trivalent lanthanide ions.

Samples with the nominal composition of $Ca_3Sc_{2-x}Y_xGe_3O_{12}$ (x=0, 0.5; 1.0; 1.5; 2.0) were synthesized by a high-temperature solid-state reaction. The starting materials of $CaCO_3$ (99.9%), Sc_2O_3 (99.9%), GeO_2 (99,9999%), and Y_2O_3 (99,9999%) were weighted out according to the nominal composition, and then grinned in an agate mortar for 30 minutes. After that, the powders were sintered at 1723 K for 18 h in air atmosphere. The phase composition of the synthesized samples was monitored by X-ray phase analysis (Bruker D8 ADVANCE diffractometer with VANTEC -1 linear detector, CuKα-radiation, the scanning step was 0.016°, and the exposure at each step was 2s). Rietveld refinement was done using the TOPAS 4.2 program. Table 1 gives our data for the solid solution in comparison with the data of [1, 2]. It is seen that, with increasing yttrium content, the cell parameters a and *V* increase. The effect of yttrium substitution for scandium on the cell parameters *a* and *V*. can be represented by the linear equations:

$$a = (12{,}5147 \pm 0{,}0046) + (0{,}1454 \pm 0{,}0037)\,x$$

$$V = (1959{,}67 \pm 1{,}93) + (69{,}87 \pm 1{,}59)\,x$$

with correlation coefficients of 0.9990 and 0.9992, respectively.

Table 1. Unit cell parameters for $Ca_3Sc_{2-x}Y_xGe_3O_{12}$ (x=0, 0.5; 1.0; 1.5; 2.0), (sp. gr. *Ia-3d*)

Parameters	*x*						
	0		0.5	1.0	1.5	2	
a=b=c, Å	12.508(48)	12.51029	12.5802(2)	12.6610(14)	12.7343(5)	12.8025(1)	12.805(8)
V, Å^3	1956.92(2)	1957.950	1990.88(11)	2029.53(7)	2065.05(5)	2098.3 (7)	2100.0(4)
References	This work	[1]	This work	This work	This work	This work	[2]

The heat capacity (C_p) of germanates $Ca_3Sc_{2-x}Y_xGe_3O_{12}$ was measured using thermal analyzer STA 449 C Jupiter (NETZSCH, Germany) by method of differential scanning calorimetry. The experiment procedure is as described earlier in [3]. The experimental results were processed using program package NETZSCH Proteus Thermal Analysis and program Sistat Sigma Plot. The experiment error did not exceed 2%. As the temperature is raised from 310 to 1000 K, C_p increases systematically. The $C_p(T)$ curves have no extrema, which can be interpreted as evidence that the garnets undergo no polymorphic transformations in the temperature range studied. The experimental data are well represented by the Maier–Kelley equation $C_p = a + bT - cT^{-2}$. For example, for

$Ca_3Sc_2Ge_3O_{12}$: $C_p = (479{,}2 \pm 0.88) + (14.67 \pm 0.90)\times 10^{-3}T - (96.99 \pm 0.88) \times 10^5 T^{-2}$,
$Ca_3ScYGe_3O_{12}$: $C_p = (482{,}2 \pm 0.58) + (17.76 \pm 0.60)\times 10^{-3}T - (90.64 \pm 0.56) \times 10^5 T^{-2}$,
$Ca_3Y_2Ge_3O_{12}$: $C_p = (491{,}7 \pm 1.27) + (18.08 \pm 1.40)\times 10^{-3}T - (92.02 \pm 1.25) \times 10^5 T^{-2}$.

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INFLUENCE OF THE INTRODUCTION OF HETEROCYCLIC MONOMERS INTO THE COMPOSITION OF POLYMERIC SUPPORTS ON THE BEHAVIOUR OF THE CATALYSTS OF CROSS-COUPLING REACTIONS

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Nowadays, the development of new palladium-containing catalytic systems is of great importance, since the reactions catalyzed by palladium are the most widespread in fine organic synthesis [1]. Among them are cross-coupling reactions such as Suzuki, Sonogashira, and Heck. It is known that cross-coupling processes have a complex mechanism, in which various processes such as aggregation, dissociation and leaching of Pd take place. This phenomenon can lead to both the formation of catalytic active species and a decrease in the activity and selectivity of catalysts [2].

In this regard, catalytic systems able to overcome the difficulties of cross-coupling processes are under constant development [3]. Highly porous aromatic polymers as supports of catalytic systems are promising since the introduction of functional groups, including heteroatoms, into the polymer composition can improve the interaction of the metal-catalyst with the substrate and the dispersion of resulting nanoparticles [4]. A number of porous aromatic polymers containing nitrogen have been synthesized from monomers such as triazine, carbazole, imine and amide blocks and are used as catalytic supports [5].

As part of this work, a one-step synthesis of amorphous porous aromatic polymers based on benzene, naphthalene, anthracene, phenanthrene, naphthol, indole, carbazole, phenanthroline, and their mixtures was carried out. The synthesis of polymers proceeded in the presence of $FeCl_3$ or $AlCl_3$ as catalysts, while 1,2-dichloroethane or methylene chloride were used as solvents. Based on the obtained polymers, Pd-containing catalysts were developed for the Suzuki, Sonogashira, and Heck cross-coupling reactions with different model compounds. It was found that the introduction of heterocycles (indole or carbazole) into the polymers' composition led to a higher conversion of aryl halides. At the same time, the introduction of phenanthrene into polymers based on indole, carbazole and naphthol negatively affected the catalytic behaviour: faster deactivation occurred at high conversions (note that the "selectivity" was almost the same in all the cases).

We found that the processes of catalyst deactivation were mainly due to the precipitation of Pd nanoparticles in the polymeric environment. It was found that the amount of cross-linking agent, as well as the presence of functional groups in the polymer composition, can affect the mean diameter of Pd nanoparticles formed during the preliminarily reduction or during the catalytic process. The catalyst stability was also influenced by the sizes of Pd nanoparticles and the relative hydrophobicity of the polymers.

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LIQUIDUS SURFACE OF T-x-y-DIAGRAM OF THE Si–Sn–As SYSTEM

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Silicon and germanium monopnictides form a family of two-dimensional layered semiconductors, and by varying the number of layers, a change in the band gap is observed [1]. Interest in bulk crystals of $A^{IV}B^{V}$ compounds is due to their ability to undergo interlayer insertion reactions. Tin and silicon arsenides SnAs, Sn_4As_3, $SiAs_2$, SiAs are suitable materials for creating electrodes for alkaline ion batteries [2, 3]. Alloying makes it possible to expand the range of practically important characteristics of the material, and from this point of view, the study of multicomponent systems formed by elements of IVA and VA groups is relevant. In this work, phase equilibria in the Si–Sn–As ternary system were studied using X-ray phase analysis (XPA), differential thermal analysis (DTA), and thermodynamic calculations.

The samples were obtained by single-temperature synthesis in evacuated quartz ampoules and annealed for 200 hours. Analysis of the results of powder X-ray diffraction allowed us to establish that subsolidus phase separation is carried out by the polythermal sections SnAs–$SiAs_2$, SnAs–SiAs, Sn_4As_3–SiAs and Sn_4As_3–Si. Based on the results of DTA and X-ray diffraction, the existence of five invariant equilibria was proven: L+As ↔ SnAs+$SiAs_2$ (850±1 K); L+$SiAs_2$ ↔ SnAs+SiAs (847±1 K); L+SnAs ↔ SiAs+Sn_4As_3 (845±1 K); L+SiAs ↔ Sn_4As_3+Si (840±1 K); L ↔ Sn_4As_3+Si+Sn (503±1 K).

Thermodynamic calculations were used to construct projections of isothermal sections of the liquidus surface of the T-x-y diagram in the regions of primary crystallization of silicon, arsenic, monoarsenide and silicon diarsenide. According to literature data, the interaction of components in the liquid phase in the binary systems Sn–As, Si–As, Si–Sn is satisfactorily described by the model of regular solutions, therefore the activity coefficients in the melt of the Si–Sn–As ternary system were calculated, also considering the melt to be a regular solution. The following values of interaction parameters in the liquid phase were used: $\alpha(\text{Sn–As}) = -14.7$ kJ/mol, $\alpha(\text{Si–As}) = -12.6$ kJ/mol, $\alpha(\text{Si–Sn}) = 30.818$ kJ/mol. There is good agreement between the calculated liquidus surface isotherms of the ternary system and liquidus temperatures in binary systems, as well as with our experimental data for most of the studied alloys, which confirms the validity of using the regular solution model. The calculation results made it possible to correct the position of monovariant curves on the plane of the concentration triangle of the T-x-y diagram of the Si–Sn–As system.

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SATURATED VAPOR PRESSURES OF PENTAERYTHRITOL ESTERS AND CARBOXYLIC ACIDS C6 OF BRANCHED STRUCTURE

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Esters of pentaerythritol and saturated carboxylic acids are widely used as highly effective base of synthetic lubricants, due to their physicochemical properties: low saturated vapor pressure and boiling points, ensuring minimal emission into the environment; low toxicity to living organisms; good lubricity. [1]

The main industrial products representing this class of compounds are esters obtained by direct esterification of pentaerythritol with saturated carboxylic acids of the C_5-C_{10} fraction, of which acids with a chain length of 6 carbon atoms make the main contribution.

In world practice, databases and approaches to modeling the characteristics of the products obtained are constantly being enriched, which require reliable experimental data on the thermophysical properties of pure compounds. An analysis of the literature indicates that for a number of pentaerythritol esters and saturated carboxylic acids C6, there are no experimental data on the phase equilibrium of liquid-vapor systems and enthalpies of evaporation.

This work aims to investigate the liquid-vapor equilibrium of pentaerythritol esters and some carboxylic acids C_6: 2,2–dimethyl butyric acid, 2-methylpentane, 4-methylpentane, 2-ethylbutane.

Pentaerythritol esters were obtained by esterification of polyol in excess of the corresponding carboxylic acids during acid catalysis. Purification of these compounds was carried out by distillation of excess carboxylic acids, alkaline washing of the catalyst and further separation by column chromatography. The purity of the studied products was at least 99% by weight (GLC control).

The determination of saturated vapor pressure values was carried out by the transpiration method, a description of this approach is given in [2].

The dependence of saturated vapor pressure on temperature was determined by the equation:

$$R \cdot ln\, p_i = a + \frac{b}{T} + \Delta^g_l C_p \cdot ln\left[\frac{T}{T_0}\right]$$

The enthalpy of evaporation at 298.2 K was determined by the equation:

$$\Delta^g_l H_{298} = -b + \Delta^g_l C_p \cdot 298.2$$

The error of the enthalpy of evaporation at a temperature of 298.2 K was estimated taking into account the error $\Delta^g_l H_{(T_{\text{cp}})}$, the contribution of extrapolation $\Delta^g_l H$ from the average temperature of the experiment to the selected reference temperature (298.2 K) and the error in calculating the change in the heat capacity of the liquid-gas transition calculated using the QSPR method [3].

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THERMODYNAMIC ANALYSIS OF CHLORINATION OF ALUMINUM OXIDE ISOLATED BY CALCINATION OF ITS HYDROXIDE

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The industrial method of aluminum production by electrolysis of cryolite-alumina melts has a number of disadvantages: high power consumption, the use of scarce fluorine salts and carbon electrodes. A promising direction that solves these problems is the chlorine method of producing aluminum, the implementation of which will make it possible to use low-quality aluminum-containing raw materials, reduce the consumption of electricity and high-quality carbon-containing electrode materials by approximately 30%. Non-consumable graphite electrodes are used in the electrolysis of aluminum chloride [1]. The creation of large-scale chlorine regeneration and practically isolated technology will ensure the use of less scarce and aggressive chlorides instead of fluorides, and will create conditions more favorable for the environment.

Nepheline concentrate is one of the promising types of non-bauxite aluminum-containing raw materials, which is processed using alkaline technology by sintering with limestone. Direct chlorination of nepheline is ineffective. In the production of aluminum using chlorine technology, rough alumina is used, which may contain 2,0-2,5% sodium aluminosilicate, and which is obtained after calcination of aluminum hydroxide isolated by the alkaline method. An additional stage of cleaning is not required in this case [2].

Thermodynamic analysis of aluminum oxide chlorination is of theoretical and practical interest and is performed for possible reactions of interaction with chlorine in the presence of a reducing agent and without it. The calculated values of the Gibbs energy (ΔG) and the equilibrium constant in the temperature range 400-1000 K show that in the presence of a reducing agent, the equilibrium of reactions is shifted towards the formation of aluminum chloride. It was found that the changes in ΔG of chlorination reactions of polymorphic modifications of Al_2O_3 increases in the series: γ-Al_2O_3, Al_2O_3-am., δ-Al_2O_3, α-Al_2O_3.

It is effectively possible to evaluate the basic patterns of obtaining anhydrous aluminum chloride based on thermodynamic characteristics and analysis of the equilibrium composition of the Al-O-C-Cl and Al-O-C-Cl-Si-Na systems with different component ratios. It was found that the optimal ratio of the starting substances during chlorination corresponds to the stoichiometry of their chemical interaction. In this case, the yield of the target products is 100% with full use of chlorine. The possibility of selective chlorination of Al_2O_3 and $SiCl_4$ has been determined. As calculations have shown, sodium oxide completely transforms into chloride, and this allows using the residue from chlorination to obtain aluminum-silicon alloys without sodium impurities.

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SUPRAMOLECULAR CATALYSIS OF ALKALINE HYDROLYSIS OF PARAOXON IN SOLUTIONS OF PIPERIDINIUM SURFACTANTS WITH CARBAMATE FRAGMENT

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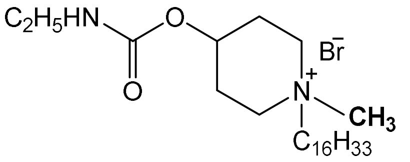
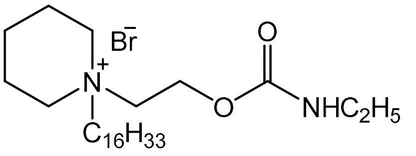
Among micellar systems used for the decomposition of organophosphorus ecotoxicants, solutions based on biodegradable surfactants occupy a special place. For the hydrolytic decomposition of the highly toxic insecticide 4-nitrophenyldiethylphosphate (paraoxon), we used supramolecular systems based on self-associating carbamate-containing piperidinium cationic surfactants with different positions of the carbamate fragment - in the para position relative to the quaternary nitrogen atom in the cycle (**4-CB(Et)-P-16**), and as a substituent at a charged nitrogen atom (**1-CB(Et)-P-16**).

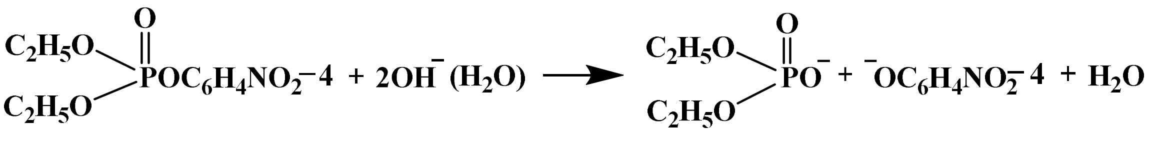


4-CB(Et)-P-16



1-CB(Et)-P-16

The micellar catalysis of alkaline hydrolysis of paraoxon (Scheme 1) in solutions of carbamate surfactants (pH=12) was studied by UV-vis spectrophotometric method.



$$(C_2H_5O)_2P(O)OC_6H_4NO_2\text{-}4 + 2OH^- (H_2O) \longrightarrow (C_2H_5O)_2P(O)O^- + {}^-OC_6H_4NO_2\text{-}4 + H_2O$$

Scheme 1

Within the framework of the pseudophase model of micellar catalysis, the threshold for surfactant aggregation in the systems under study (critical micelle concentration) and quantitative characteristics of the micellar-catalyzed process were determined: binding constants of the reagents, i.e. substrate (phosphate) and nucleophile (hydroxide ion), with surfactant aggregates and the reaction rate constant in the micellar pseudophase. The determining role of the factor of reagents concentration in micelles in the catalytic effect has been established. The dependence of the catalytic effect of the systems under study on the position of the carbamate fragment in the piperidinium ring of the surfactant is shown.

The work was carried out with financial support from the Russian Science Foundation, grant N 23-73-10033.

DEPENDENCE OF GIBBS FREE ENERGY ON SURFACE TENSION DURING THE FORMATION OF FIREFIGHTING FOAM BUBBLES

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Determination of the direction of spontaneous foam formation and degradation process is possible using Gibbs free energy. [1].

In differential form, the equation for calculating the change in Gibbs free energy [2] has the following form (1).

$$dG = -Sd(T) + \sum V_i d(p_i) + \sigma d(A) \qquad (1)$$

When calculating the change in Gibbs free energy, the possibility of foam formation with monodisperse bubble size distribution was considered for 1 m^3 of air used, with an average foam bubble diameter of 1mm - 20mm.

The obtained values of the Gibbs free energy are in the positive region. The Gibbs free energy decreases with increasing diameter of foam bubbles, which shows the shift of equilibrium in foam formation towards the formation of large foam cells with its subsequent settling.

When the surface tension of the solution decreased from 32 mN/m to 18 mN/m, a significant decrease in the change in Gibbs free energy formation was observed (Figure 1), which shows greater stability of the foams with decreasing surface tension.

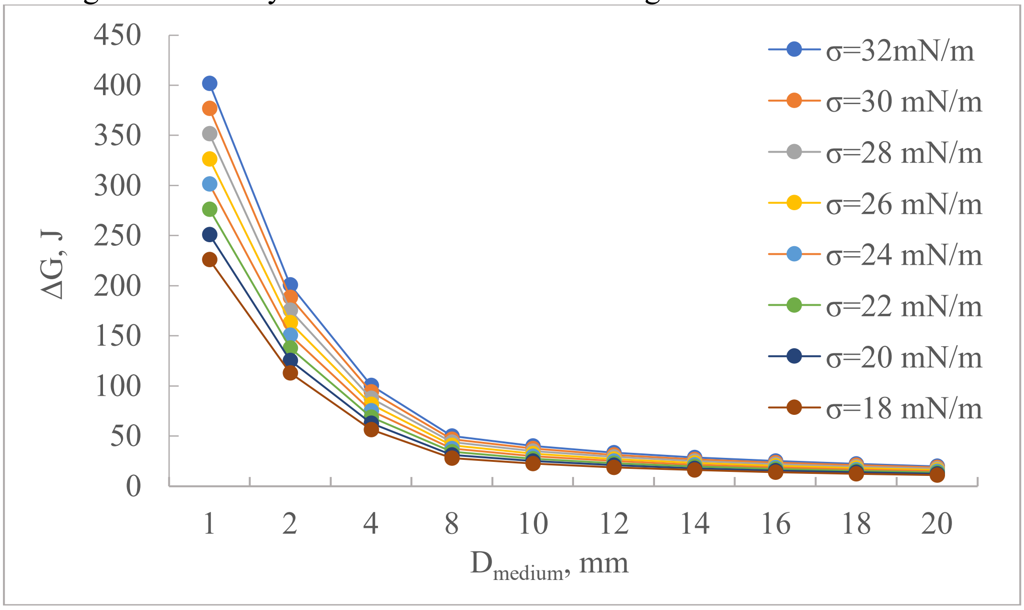

Figure 1. Dependence of the change in Gibbs free energy during the formation of firefighting foam bubbles (p=101325 Pa, T=293 K), when varying the surface tension of foam

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INFLUENCE OF STABILITY CONSTANTS OF METAL-CARBOXYLATE COMPLEXES ON SPECTRAL SHIFTS OF SILVER NANOPLATES MONOLAYER

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Earlier, we demonstrated how local refractive index and thickness of the shell impacted the spectral shifts of localized surface plasmon resonance (LSPR) of silver nanoplates (AgNPls) [1]. But surface charge of ligand layer also affects LSPR peak position and requires investigation. We deposited AgNPls onto thin transparent acrylate films as published earlier [2] and treated the monolayer with 3-mercaptopropionic acid (MPA). After the film was immersed in 0.1 M N-morpholinoethanesulfonate buffer pH 6, aliquots of aqueous Me^{n+} salts were injected (c_{Me}=1 mM). To find quantitative correlations, we plotted LSPR spectral shifts in extinction spectra of AgNPls monolayer versus $\log K_1$ of acetate complexes with corresponding cations [3], which we supposed to be analogous to complexation to MPA in monolayer (Figure 1).

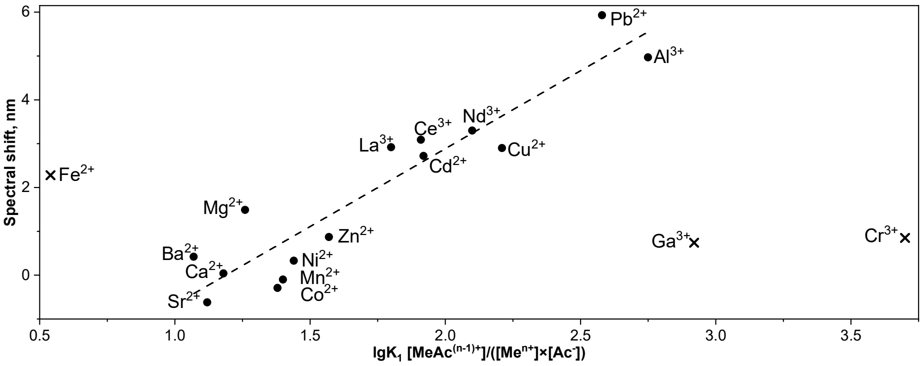

Figure 1. LSPR spectral shifts of monolayers of MPA-stabilized AgNPls induced by Me^{n+} versus $\log K_1$ of acetate complexes of corresponding cations.

Magnitudes of Me^{n+}-induced spectral shifts are close for Me^{2+} and Me^{3+}, probably due to hydrolysis of the latter. $\log K_1$ for Fe^{2+}, Ga^{3+}, Cr^{3+} were obtained by different methods, so they were not taken into consideration. Transition metal cations induced stronger shifts comparing to alkaline earth Me^{2+}, excluding Mn^{2+}, Co^{2+} and Ni^{2+}. Stronger shift for Fe^{2+} is probably due to presence of oxidized Fe^{3+} in the solution. The shifts are driven by ionic mechanism, in which the double electrical layer of MPA is altered in the presence of Me^{2+}, but for the first time we demonstrated ion-specific spectral shifts.

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TENSION FORMATION AND CHANGES IN SPECIFIC SURFACE AREA OF STYRENE-DIVINYLBENZENE COPOLIMERS INCLUDING METAL-COMPOSED AT DIFFERENT TEMPERATURES

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Based on a combination of TG-MS, IR, XPS and low-temperature nitrogen adsorption methods, the limits of permissible non-oxidative thermal effects on styrene-divinylbenzene copolymers have been studied and justified. The transformation of functional groups of industrial styrene-divinylbenzene copolymers MN100 and MN270 in the temperature range up to 300 °C has been studied. A single macromolecule of styrene-divinylbenzene copolymer, as well as a copolymer filled with palladium clusters, was simulated by molecular dynamics. Changes in the strength of the polymer structure, as well as changes in the specific surface area of the polymer and the metal-filled polymer in temperature range of 77-723 K were studied.

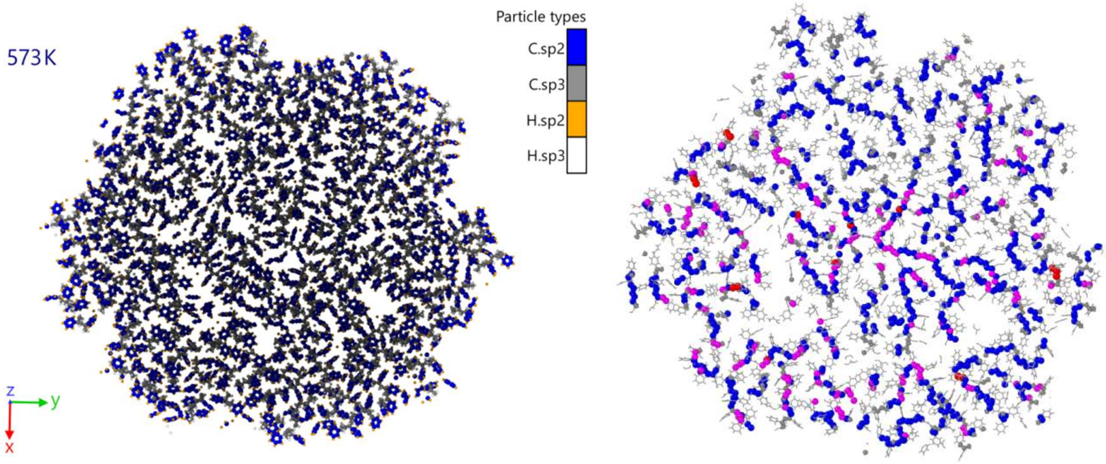

Figure. Copolymer molecule slice and σ-bond tension distribution of alkane part of polymer at 573 K

The study shows that tension developing in the polymer network at increasing temperature clusters and involves divinylbenzene bridges. The development of tension is quantified depending on temperature. The changes in the specific surface area of the polymer, as well as the polymer containing about 1% by weight of metal clusters, are not identical with temperature changes. Metal clusters were shown to act as local sites of stiffness of the polymer network in a wide temperature range.

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THERMOGRAVIMETRIC ANALYSIS OF WOOD WASTE

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Wood processing is a prospective way to minimize the waste of forestry and woodworking industries. Nowadays, different methods are used for wood waste processing: combustion, pyrolysis, liquefaction, torrefaction, carbonization etc [1, 2]. These methods are applied for the obtaining of valuable chemicals, combustible gases, and biochar. Despite the thermochemical methods (pyrolysis, carbonization, torrefaction) are considered to be the most efficient methods for waste utilization, the systematic studies are required for the proper technology development [3]. Thermogravimetric analysis is one of the major methods used to study the thermal decomposition of biomass. The thermogravimetric data collection for the different types of biomass waste is an important task. It is known that the rates, mechanisms as well as the product yields of biomass thermal decomposition strongly depend on the type of the feedstock, the vegetation area and conditions, and on the part of the plants.

In this work the thermal decomposition of wood waste was studied in a temperature range of 25-1000 °C by a thermogravimetric analysis using TG 209 F1 NETZSCH (Netzch Group, Germany) equipped by the mass-spectrometer device Aelos CSM 403 P (Netzch Group, Germany). For types of wood waste were studied: pine and birch sawdust, and pine and birch bark.

The analysis of the thermogravimetric data showed that for the both types of sawdust five peaks with different intensity can be observed on the differential thermogravimetric curves. The first peak at 49 °C corresponds to the vaporization of the residual humidity and extractives. The second peak at ca. 213 °C can be related to the partial decomposition of hemicelluloses. Peak at ca. 351 °C corresponds to the decomposition of cellulose. Two peaks at ca. 286-300 °C and 410 °C can be related to the decomposition of lignin. The main weight loose (about 79 wt. %) is observed in the temperature range of 200-600 °C. At temperatures higher than 600 °C the significant decomposition was not noted.

For the wood bark, the main peaks on the differential thermogravimetric curves were noted to be ca. 86 °C, 317 °C, 370 °C, 413 °C. These peaks can be related to the decomposition of main components of bark: extractives, cellulose, and lignin. The main weight loose (about 65 wt. %) is observed in the temperature range of 250-500 °C.

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THERMAL DECOMPSITION OF WOOD BARK IMPREGNATED WITH SILANES. THERMOGRAVIMETRIC ANALYSIS

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Carbon materials are widely used in catalysis. Carbon is considered to be a promising support for the deposition of metals, metal phosphides, metal sulphides etc. because of their high specific surface area, resistance to acidic or basic media, amphoteric character, high-temperature stability, tailored pore size distribution, the ability for modification, and cheapness [1]. The carbon obtained from the biomass have gain an attractive attention last years because of the availability and cheapness of the feedstock [2]. Biochar is characterized by high porosity with a hierarchical structure. For the production of biochar different methods are widely used: pyrolysis (both slow and fast), torrefaction, dry and wet carbonization. The las one is called hydrothermal carbonization [4]. The composition, structure, morphology, and textural properties of carbon materials strongly depend on biomass type, preparation method used, temperature, size of the particle, heating rate, residence time, etc.

Despite the high level of the development of carbonization technologies of biomass for biochar production, novel techniques are applied to form additional functional groups, structures and properties of biochar. One of such methods is a preliminary treatment of biomass before the carbonization. For a preliminary treatment the wetness impregnation with solutions of alkali, metal salts etc. are widely used. To form the additional porosity and strength of biochar in this work we decided to impregnate the initial feedstock with the solutions of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES). The further thermal decomposition of the samples was studied in a temperature range of 25-600 °C by a thermogravimetric analysis using TG 209 F1 NETZSCH (Netzch Group, Germany). The decomposition of the impregnated birch and pine bark was studied. The initial bark was found to contain extractives (14.5 and 24.1 wt. %), hemicelluloses (18.1 and 26.8 wt. %), cellulose (48.8 and 45.3 wt. %) and lignin (29.2 and 25.1 wt. %) for pine and birch bark respectively. In all cases, the addition of the silanes led to an increase in the residual weight forming the carbon-silica containing materials. The addition of the silanes did not have any catalytic effect on the thermal decomposition of the wood bark. The last was confirmed by the unchanged temperature peaks on the differential thermogravimetric curves related to the main components of the feedstock. However, the joint thermal decomposition of the silanes and cellulose was proposed.

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TEMPERATURE AND PHASE TRANSITIONS IN COPOLYARYLENE ETHER KETONES BASED ON HYDROQUINONE

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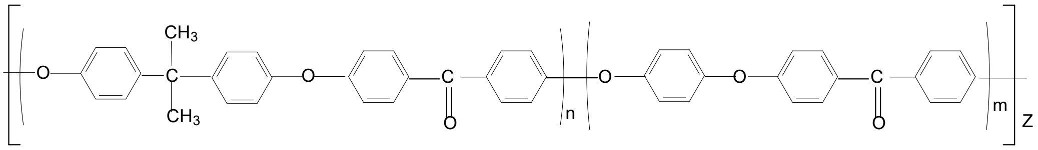
The paper presents the results of a study of temperature and phase transitions of copolyarylene ether ketones (Co-PAEK) based on 1,4-dihydroxybenzene and 4,4′-dioxydiphenylpropane of the formula:



Co-PAEK was synthesized by high-temperature polycondensation using the nucleophilic substitution mechanism [1, 2].

The properties of Co-PAEKs are determined by the chemical composition, crystal structure of the polymer, temperature conditions of processing and, above all, the ratio of ether (-O-) and carbonyl (C=O) groups.

The glass transition and melting temperatures, as well as the degree of crystallinity of the samples found by differential scanning calorimetry, are summarized in the table.

Table - Differential scanning calorimetry data

co-PAEK based on:	Tg ^0C	T_{melt} ^0C	C_p, Дж/г	α, %
1,4-dihydroxybenzene	151	336	0,15	44,3
co-PAEK-25	132	282	0,143	22,7
co-PAEK-50	138	-	0,332	-
co-PAEK-75	135	-	0,249	-
4,4′-dioxydiphenylpropane	152	-	0,34	-

where: co-PAEK-25, co-PAEK-50, co-PAEK-75 are co-PAEK with a content of 25, 50 and 75 wt.% 4,4′-dioxydiphenylpropane respectively.

The study showed that with copolymers the content of ether bonds decreases from 11.1% to 7.9%, the content of keto groups - from 9.7% to 6.9%. At the same time, the ratio of ether groups to keto group remains constant and is 0.87. The Tg of these polymers, depending on the composition and ratio of the initial dioxy compounds, lies in the range of 130-155°C, the temperature of the onset of destruction is above 400°C.

Depending on the composition, co-PAEKs are semicrystalline or amorphous. Co-PAEK containing 50% wt. and more are amorphous. This fact was also confirmed by X-ray phase analysis. It has been shown that many of the performance properties of co-PAEK depend on the composition.

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DIELECTRIC MIE-RESONANCE OF a-Se NANOSTRUCTURES AS AN INSTRUMENT FOR PHOTOCATALYSIS ENHANCING

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Amorphous selenium nanostructures of submicron size exhibit pronounced dielectric Mie-resonances with high extinction cross-section, low optical losses and a tunable spectral position in the visible and near-infrared region [1]. Combining a capability of photogenerating electron-hole pairs and the effect of Mie-resonances allows considering selenium nanoparticles (NPs) as a promising material with enhanced photocatalytic activity. Moreover amorphous structure of selenium nanomaterials results in increased lifetime of photogenerated charge carriers, which also promotes photocatalysis. Here, we demonstrate how colloidal a-Se and a-Se/Ag_2Se NPs of 200 nm with Mie-resonance modes in the visible region (Figure 1a) influence on the rate of photo-redox processes with ferrocyanide complexes.

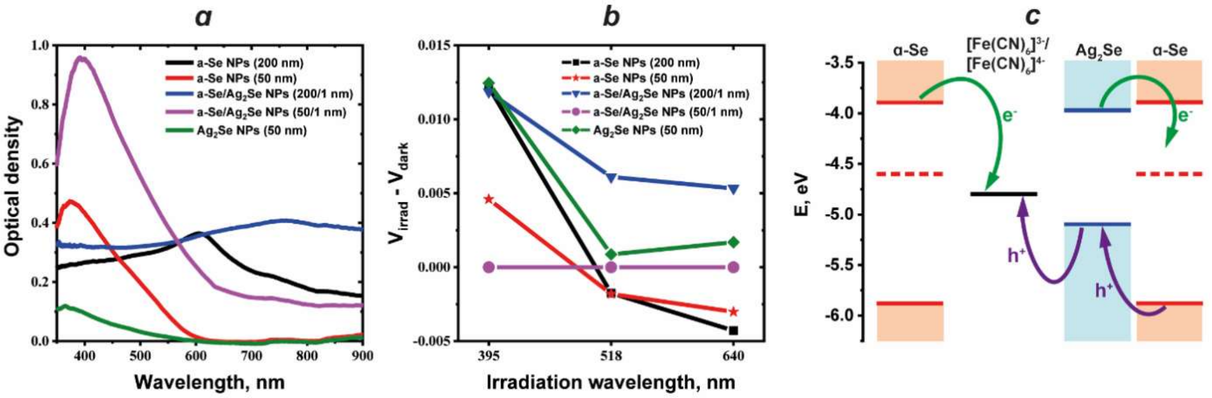

Figure 1. Extinction spectra of colloidal NPs, used in the kinetic experiments (a); dependence of $[Fe(CN_6)]^{4-}$ photooxidation rate on irradiation wavelength (b); schematic energy diagram for proposed mechanism of ferrocyanide complexes redox transformations, photocatalyzed by a-Se and a-Se/Ag_2Se NPs (c).

To identify the influence of dielectric Mie resonances on the rate of the photo-redox processes we used reference samples of α-Se and α-Se/Ag_2Se NPs (50 nm) and Ag_2Se NPs (50 nm), which do not exhibit Mie-resonances (Figure 1a). Aqueous colloidal solutions of NPs (1.3 mL), purified by dialysis, were studied in the presence of 1 mg/ml polyvinylpyrrolidone (M_w = 350000) and 1 mM $K_4[Fe(CN_6)]$. The total surface area of NPs in the solutions was constant in all experiments. Kinetic experiments were carried out with constant stirring in the dark or under LEDs illumination at wavelength of 395 nm, 518 nm, 640 nm. The extinction spectra of the solutions under study were measured every 10 min to determine the optical density at the maximum of $[Fe(CN_6)]^{3-}$ absorption band (425 nm). The data obtained was used to plot kinetic curves and calculate the rates of $[Fe(CN_6)]^{4-}$ oxidation (Figure 1b). An increase in the efficiency of $[Fe(CN_6)]^{3-}$ photoreduction upon photoexcitation of dielectric resonances in α-Se NPs (200 nm) was revealed. α-Se/Ag_2Se NPs (200 nm) exhibit photocatalytic activity enhanced by dielectric resonances in the photooxidation of $[Fe(CN_6)]^{4-}$. In the Fig. 1c the thermodynamically possible route of the studied photocatalytic processes is proposed.

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THERMODYNAMIC MODELING OF PHASE EQUILIBRIA IN THE Bi-Ga-Zn SYSTEM

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The Bi-Ga-Zn system is a subsystem of the Bi-Ga-Sn-Zn system, alloys of which are promising as high-temperature heat transfer agents in concentrated solar power. Profound knowledge of phase equilibria in the Bi-Ga-Sn-Zn system is necessary to use such alloys. This in turn requires knowledge of thermodynamic models (analytical expressions for the Gibbs energy) of all phases existing in this system, including those of the Bi-Ga-Zn subsystem. Thermodynamic modeling of the Bi-Ga-Zn system has not been carried out yet.

Experimental studies of the thermodynamic properties of liquid and phase equilibria in this system were performed in [1,2]. These data and available thermodynamic descriptions of the Bi-Ga, Bi-Zn, and Ga-Zn binary systems were used to build a thermodynamic model for the liquid phase of the Bi-Ga-Zn system. The model and those of other phases were used to determine coordinates of the invariant points of the Bi-Ga-Zn system and the projection of its liquidus surface. The isothermal cross section of the system's phase diagram at 573 K and the polythermal cross section for $x_{\mathrm{Bi}}/x_{\mathrm{Zn}} = 1$ were calculated by minimizing the Gibbs energy of the system. The calculated liquidus surface projection of the Bi-Ga-Zn system is presented on Figure. The bold lines represent monovariant equilibria; the thin lines, liquidus isotherms at 473-623 K. The letter E refers to the composition of eutectic liquid; M' and M'', to the composition of L' and L'' liquids in monotectic equilibrium. (Bi)' and (Zn)' denote areas of the primary crystallization of Bi and Zn from liquid L' depleted of Ga; (Bi)'' and (Zn)'', crystallization from liquid L'' enriched with Ga; (Bi)''' and (Zn)''', crystallization from L'+L'' two-phase regions.

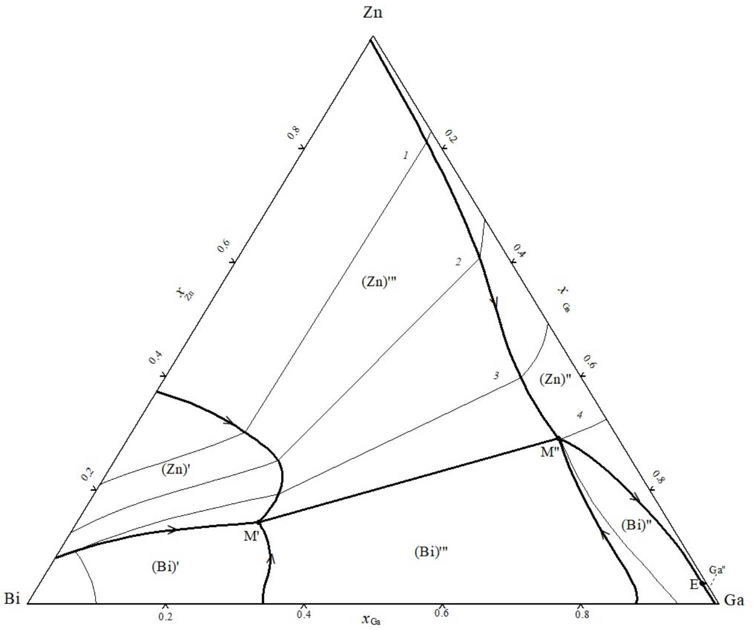

Figure. Calculated projection of the liquidus surface of the Bi-Ga-Zn system. Isotherms: 623 K (*1*), 573 K (*2*), 523 K (*3*), 473 K (*4*).

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DESCRIPTION OF THE PHASE EQUILIBRIUM OF AMMONIA IN A GAS-LIQUID SYSTEM

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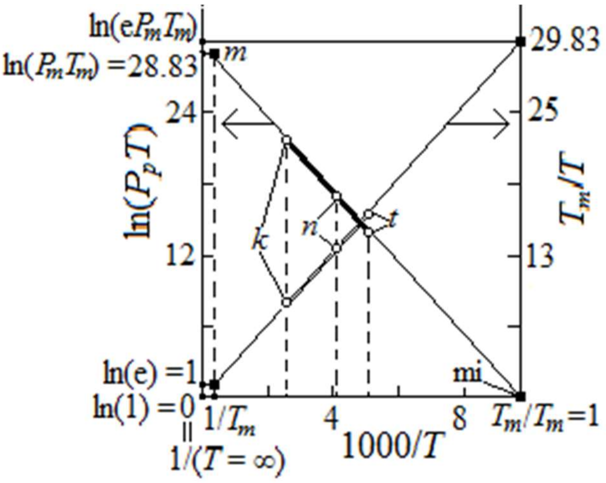
The purpose of the message is to show a refined equation with two coefficients-parameters (P_m at T_m at point m) [1-5] – $(P_p/P_m)\times(T/T_m)\times\exp(T_m/T -1) = 1$, where P_p and T are the equilibrium parameters applicable to substances in macro- and micro-systems gas-liquid (GL) and gas–solid. For the initial equation, presented in logarithmic form – $\ln(P_pT) = \ln(eP_mT_m) - T_m/T + \ln(1)$. The parameters T and P_p, in coordinates $\ln(P_pT)$ – 1/T, form a straight line, as shown (Figure) by the example of ammonia [6] in a gas-liquid (GL). On the abscissa, zero corresponds to the value $0 = 1/(T = \infty)$, on the ordinate – $0 = \ln(1)$, but $\infty\times0 = 1$.



The parameters T_m and P_m are calculated from two arbitrary points (P_1 at T_1 and P_2 at T_2) according to the equations: $T_m = (1/T_1 - 1/T_2)^{-1}\times\ln[(PT)_2/(PT)_1]$, $P_m = (PT)_1/T_m)\times\exp(T_m/T_1 -1)$. For the minimum values of the equilibrium parameters, T_{mi} and P_{mi} at the mi point have $\ln(eP_mT_m) - T_m/T_{mi} = \ln(P_{mi}T_{mi}) = 0$, and therefore $T_{mi} = T_m/\ln(eP_mT_m)$. When $\ln(P_{mi}T_{mi}) = 0$, they have $P_{mi}T_{mi} = 1$, and therefore for P_{mi} they get P_{mi} (Pa) = $1/T_{mi}$ (1/K). For ammonia in the GL system, the parameters are set for the limit points (m and mi): T_m = 3080.5 K, P_m = 1.078×109 Pa, T_{mi} = 103.26 K, $P_{mi} = 9.684\times10^{-3}$ Pa.

The heat of phase transformation of one mole (ΔQ, J/mol) and one ammonia molecule ($\Delta q = \Delta Q/N_a$, J/K; N_A is the Avogadro number) is related to the temperature T (in exponential function) by the equality – $(T_m/T -1) = \Delta Q/RT = \Delta q/kT$, where $k = R/N_A$ (J/K). (In Fig. points: t – triple, k – critical, n – at P_p = 101325 Pa).

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DESCRIPTION OF THE CHEMICAL EQUILIBRIUM OF AMMONIA

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It is shown that the phase and chemical equilibrium in gas-liquid and gas-solid systems can be described by an equation with coefficients T_m and P_m [1-3] – $P/P_m = (T_m/T)\times e^{(1-T_m/T)}$ or $\ln(eP_mT_m) = \ln(PT) + T_m/T$; the equilibrium parameters (T and P) in coordinates ln(PT) – 1/T form a straight line. The purpose of the report is to use the example of ammonia synthesis to show the application of an equation with two coefficients in describing chemical equilibrium in the gas phase.

If the equilibrium fraction of the mass of ammonia in the gas mixture (α) is used as the ratio $(1-\alpha)/\alpha = 1/\alpha - 1$, then in the coordinates $\ln(1/\alpha - 1) - 1/T$, the equilibrium parameters form a straight line with a break at $(1-\alpha_x)/\alpha_x = 1$ or $\alpha_x = 0.5$ for $T = T_x$. This is shown in the figure according to data [4] in the temperature range from 298.15 K to 1500 K at a total pressure $P_n = 101325$ Pa and $100\times P_n$.

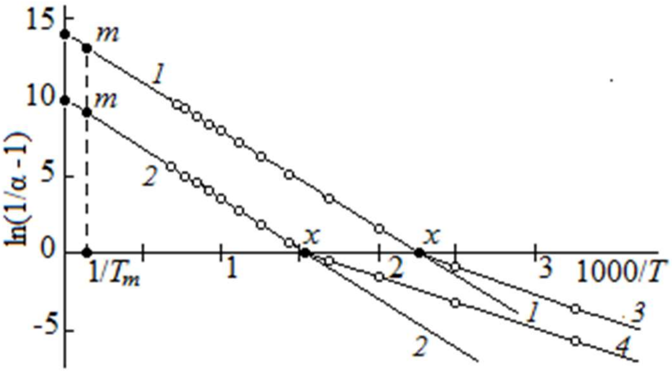

Figure. Chemical equilibrium of NH_3 according to [4] in the coordinates shown: 1 and 3 – at pressure P_n, 2 and 4 – at $100\times P_n$; m – points at $T = T_m$, x – points for a_x at T_x.

For lines *1* and *2* in the range from $1/T_m$ to $T_m/T_m = 1$, [2] values of the coefficients-parameters – $T_m = 6305.0$ K and $P_m = 5.873\times10^{10}$ Pa were obtained, which corresponds to the reaction of $½(3H_2 + N_2) = NH_3 \pm \Delta Q$, where $\Delta Q = R(T_m - T)$, J/mol. At $\ln(1/\alpha - 1) = 0$, the fracture of lines *1* and *2* is due to a decrease in the number of synthesis gas molecules; for lines *3* and *4* (below the abscissa) the values of the coefficient parameters turned out to be half as much. Under standard conditions, for the heat of formation of one mole of ammonia (ΔQ_{25}, J/mol), according to the equation shown, $Q_{25} = 49.94$ kJ/mol is obtained (the reference value of the enthalpy of formation $\Delta H_{25} = 46.22$ kJ/mol).

The proposed equations are applicable to macro- and micro-systems; the heat of formation of one ammonia molecule at T is $\Delta q = \Delta Q/N_A$ (J), where $N_A = 10^{23.7798} = e^{54.7549}$ is the Avogadro number or mol (exponentially a power number with base 10 or e).

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INVESTIGATION OF THE As_2Te_3-HoTe SYSTEM

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It is known that antimony telluride As_2Te_3 occupies an important place among semiconductor thermoelectric materials[1,2]. However, the relatively narrow range of operating temperatures, low melting point and mechanical strength of this compound and thermoelectric materials based on it limit the possibilities of their application. The introduction of heavy atoms of rare earth elements into the crystal lattice can lead to an improvement in the thermoelectric properties of such materials.

The development of the novel preparative methods for direct synthesis of functional materials requires to provide an accurate study of phase relations and plot the phase diagram[3].

This work is a continuation of our studies of phase relations in the Ho-As-Te system[4]. The alloys of the studied system were synthesized by melting of high purity elements (arsenic, CAS 7440-38-2; tellurium, 13494-80-9, holmium, 7440-60-0) in evacuated (~10^{-2} Pa) quartz ampoules at 600-1100 K for 6 hours with following thermal annealing at 700 K to achieve an equilibrium state.

X-ray powder diffraction (XRD) and differential thermal analysis (DTA) were employed to analyze the samples in order to plot the phase diagram.

Based on results obtained a phase diagram of the As_2Te_3-HoTe system was constructed (Figure 1).

It was established that the system belongs to the simple eutectic type. The eutectic coordinates are 70 mol% As_2Te_3 and 615 K. Solubility based on the As_2Te_3 is 5 mol% at 615 K and with decreasing temperature, the solubility decreases and reaches 3 mol% at 300 K.

XRD data confirmed the constructed phase diagram.

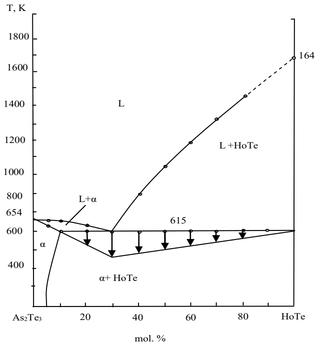

Figure 1. Phase diagram of the As_2Te_3-HoTe system.

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THERMODYNAMIC ANALYSIS OF THE ETHYLENE BIOMIMETIC MONOOXIDATION PROCESS

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The new highly efficient method has been developed for the production of ethyl alcohol and acetaldehyde by gas-phase monooxidation of ethylene in the presence of hydrogen peroxide on the heterogeneous biomimetic catalyst, per-FTPhPFe^{3+}OH/Al_2O_3, which has high resistance to oxidizing agents and high temperatures, as well as a long service life. The yield of ethyl alcohol and acetaldehyde obtained by this oxidation method with high selectivity were 15.4 and 34.6 wt.%, respectively. From experimental kinetic patterns follows that the conversion of ethylene into monooxygenase products occurs in the following sequence: $C_2H_4 \xrightarrow{H_2O_2} C_2H_5OH \xrightarrow{H_2O_2} CH_3CHO$. Each of these transformations is a complex reaction and consists of two coherent-synchronized reactions: 1) primary (catalase) and 2) secondary (monooxygenase and peroxidase) reactions.

Catalase reaction:

$$H_2O_2 + H_2O_2 = 2H_2O + O_2 + 207.92\,kJ/mol \qquad (I)$$

Monooxygenase reaction:

$$H_2O_2 + C_2H_4 = C_2H_5OH + {}^{1}\!/_{2}O_2 + 148.08\,kJ/mol \qquad (II)$$

Peroxidase reaction:

$$H_2O_2 + C_2H_5OH = CH_3CHO + 2H_2O + 315.08\,kJ/mol \qquad (III)$$

The calculated values of the thermal effects of catalase, monooxygenase and peroxidase reactions (I) - (III) showed that stage (III), the peroxidase reaction, is much more exothermic than monooxygenase reaction (II). We may therefore assume that the stage of ethyl alcohol formation from ethylene is probably limiting.

The kinetic investigation of ethylene monooxidation process was carried out [1] and the thermodynamic parameters of this reaction were calculated. Having the values of the pre-exponential factor for the reaction of the mimic-substrate complex formation using the equation: $A^* = (kT/h)\exp(\Delta S^*/R)$ activation entropy ΔS^* values were determined. Further according to the ratio: $\Delta H^* = \Delta G^* + T\Delta S^*$ activation enthalpy values were obtained (Table). Using the Gibbs equation: $\Delta G^* = -RT\cdot 2.3\lg k_S$ the values of free activation energy (Gibbs energy) were calculated (Table).

Table.

T, K	**$k_{eff}\times 10^7$ $sm^3\cdot s/mol$**	**E_{eff}, kJ/mol**	**$A_{eff}\cdot 10^5$**	**$-\Delta G^*$ kJ/mol**	**$-\Delta S^*$ kJ/(mol·K)**	**$-\Delta H^*$ kJ/mol**
413	4.54	42.0	0.178	25.26	0.115	72.75
433	8.33			28.34	0.116	78.57
473	12.5			32.65	0.117	87.99

As can be seen from the table, the thermodynamic analysis of the process of ethylene biomimetic oxidation with hydrogen peroxide made it possible, without resorting to labor-intensive experiments, to identify the limiting stage of the process and change the direction of the reaction towards obtaining a higher yield of the target product.

VOLUME PROPERTIES OF BROMIDE AMMONIUM SOLUTIONS IN MIXED SOLVENTS N-METHYLPYRROLIDONE–WATER AT 298.15 K

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In this work, we continue systematic studies of the thermodynamic properties of solutions based on an aprotic dipolar solvents [1–3]. Data on the properties of the N-methylpyrrolidone (MP) –water system [4] are evidence of specific interactions of its components with the formation of associates of the composition $MP\cdot 2H_2O$, which should influence the properties of ternary systems. Studies of solutions in mixed solvents is of theoretical and practical interest, because the majority of chemical processes are conducted in such systems.

The densities (ρ) of solutions of ammonium bromide in MP–water mixtures were measured at 298.15 K over the entire range of mixed solvent compositions. The density of solutions was measured on a precision Anton Paar DMA 4500 densimeter with a temperature control accuracy of $\pm 5\cdot 10^{-3}$ K. The error in measuring ρ of solutions was $\pm\ 5\cdot 10^{-5}$ g·см$^{-3}$.

The data obtained were used to calculate the apparent molar volumes (Φ_V) of ammonium bromide in MP-water mixtures. To determine the standard partial molar volumes of ammonium bromide in MP–water mixtures at infinite dilution $\overline{V_2^0} = \Phi_V^0$, the dependences $\Phi_V = f(m^{1/2})$ were approximated by linear regression equations. The values obtained for ammonium bromide in MP –water mixtures are listed in Table.

Table. Standard partial molar volumes of ammonium bromide in MP−water mixtures at 298,15 K

X_{MP}	0,1	0,3	0,5	0,75	0,9	1,0
$\overline{V_2^o}$, cm^3·mole^{-1}	44,8	42,9	39,5	35,0	33,0	32,9[2]

For NH4Br, as for the alkali metal halides [3], the dependences on the composition of the mixed solvent pass through the maximum, however, for ammonium halides its position is shifted to the region of lower MP content. This indicates the complex nature of intermolecular interactions in the studied solutions, which is significantly influenced by both ion parameters and properties of the MP-water binary system.

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STANDARD PARTIAL MOLAR VOLUME OF AMMONIUM SUCCINATE IN AQUEOUS SOLUTION AT 298.15 K

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Succinic acid and its salts, in particular ammonium succinate, are widely used in modern pharmaceuticals [1,2]. The limited availability of reliable data on the thermodynamic properties of ammonium succinate determined the purpose of the study: measuring the density of aqueous solutions of $C_2H_4(COONH_4)_2$ and determination of the standard partial molar volume of ammonium succinate.

Ammonium succinate was obtained by neutralization of succinic acid with a mixture of ammonia solution and ammonium carbonate. The homogeneous solution was kept for 1 hour at room temperature and evaporated under vacuum. The viscous mass was cooled, washed with ethanol and crystallized. The crystalline product was washed with ethanol, filtered and dried. The resulting ammonium succinate was recrystallized twice from bidistillate and absolute ethanol, dried for 3-4 hours at 343 K in air and 48 hours in vacuum at 333 K. The content of the basic substance determined by the photometric method was at least 99.8 wt. %. The structure was confirmed by IR spectroscopy and a high degree of purity of the salt sample was established. The densities (ρ) of aqueous solutions of ammonium succinate were measured at 298.15 K. The density of solutions was measured on a precision Anton Paar DMA 4500 densimeter with a temperature control accuracy of $\pm 5\cdot10^{-3}$ K. The error in measuring ρ of solutions was $\pm 5\cdot10^{-5}$ g·cм$^{-3}$.

The data obtained were used to calculate the apparent molar volumes (Φ_V) of $C_2H_4(COONH_4)_2$ in water. To determine the standard partial molar volumes of ammonium succinate at infinite dilution $\overline{V_2^0} = \Phi_V^0$, the dependences $\Phi_V = f(m^{1/2})$ were approximated by linear regression equations. The calculated value is shown in the table. The separation of the value into ionic components was carried out using the literature data on the value for ammonium ion in water [3] and based on the condition of additivity of partial molar values. The calculation results are presented in Table.

Table. Standard partial molar volumes of ammonium succinate, NH_4^+ and $C_2H_4(COO)^{2-}$ ions in aqueous solution at 298.15 K

	$C_2H_4(COONH_4)_2$	NH_4^+	$C_2H_4(COO)_2^{2-}$
$\overline{V_2^o}$, cm^3·mole^{-1}	62,0± 0,2	23,5± 0,1 [3]	15,0± 0,2

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The research was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of the scientific project of the Laboratory of Ionic Materials (LIM), project No. FSSM-2024-0006.

THERMAL BEHAVIOR OF TRIS(3-FLUOROPHENYL)ANTIMONY DIHALIDES AS POTENTIAL PRECURSORS TO A RANGE OF FUNCTIONAL MATERIALS

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Antimony (V) organometallics are widely used in different fields of human activity as reagents of organic synthesis, components of catalyst, oil additives, materials for optoelectronic (organic light-emitting diode or solar cell), for fixation of carbon dioxide, as fungicides (for agriculture) or biocides (in medicine). The most significant clinical use of antimony organic complexes is in the treatment of various diseases (leishmaniose, cancer and hepatitis C). Therefore, the synthesis of new organic antimony derivatives and investigation their physicochemical properties will expand the range of compounds with useful properties.

The current work ascribes the study of the thermal properties, vapor phase composition for tris(3-fluorophenyl)antimony dihalides $(3\text{-}FC_6H_4)_3SbX_2$ (X = F (**1**), Cl (**2**), I (**3**)). Samples of antimony complexes 1-3 were prepared following the synthetic methods [1]. Tris(3-fluorophenyl)antimony difluoride (1) was obtained in the exchange reaction between tris(3-fluorophenyl)antimony dichloride and sodium fluoride. Tris(3-fluorophenyl)antimony dichloride (2) and diiodide (3) were obtained by the reaction of tris(3-fluorophenyl)antimony with chlorine and iodine in benzene. Molecular structures of the complexes established with X-ray diffraction analysis.

The phase transitions of the complexes 1-3 was investigated on a DSC204F1 “Phoenix” (“Netzsch”, Germany) in the temperature range 293-673 K. A thermogravimetric study of 1-3 was performed utilizing a Mettlet Toledo TGA/DSC 3+ (“Mettler Toledo”, Switzerland) in the temperature range 293-953 K. The phase composition of thermolysis products 1-3 was carries out by X-ray phase analysis. The vapor phase composition of 1-3 was investigated on a Polaris Q/Trace GC Ultra chromatomass spectrometer with an ion mass analyzer (Thermo Electron Corporation, USA).

According to present research all studied compounds demonstrate thermal stability, have melting (lower 423 K), decomposition (higher 473 K) and the good correspondence of the composition of vapor phase to the molecular formulas.

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THERMODYNAMIC OF SYN-GAS ABSORPTION IN DODECANE

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The absorption of synthesis gas in liquid media is one of the major parameters necessary for the interpretation of the kinetics and phase equilibria for Fischer-Tropsch synthesis. Moreover, the solubility data for H_2 and CO in the hydrocarbons are required to understand the reaction mechanisms. The absorption of the synthesis gas strongly depends on the process conditions, nature of absorbent, and the interaction between the syn-gas molecules and hydrocarbons. The data on the solubility and phase equilibria of CO and H_2 are available in the literature, but all studies were carried out at a low temperature and pressure (25-150 °C, 0.1-1.5 MPa).

In this work, the data on the solubility for both CO and H_2 absorption in dodecane at high temperature (100-300 ºC) and pressure range (1.0-5.0 MPa) are reported. The study of the gas solubility was carried out in the developed set-up containing the high-pressure batch reactor and a drop-meter. The thermodynamic parameters were calculated based on the solubility data (Table 1).

Table 1 – Thermodynamic parameters of syn-gas absorption in dodecane

Parameter		Individual gas		Gas mixture	
		CO	H_2	CO	H_2
n-dodecane	Activation energy of absorption, kJ·mol^{-1}	13.8±0.2	54.6±0.6	3.8±0.2	8.1±0.2
	Enthalpy of absorption, kJ·mol^{-1}	+13.6±0.4	-4.4±0.3	-2.9±0.3	-7.2±0.2
	Henry constant, MPa	0.9±0.2	0.9±0.2	5.1±0.2	5.2±0.2

The calculation of the constant of the phase equilibrium was carried out using Soave-Redlich-Kwong cubic equation. The visualization of the process conditions effect on the gas-liquid equilibrium is shown in Figure 1.

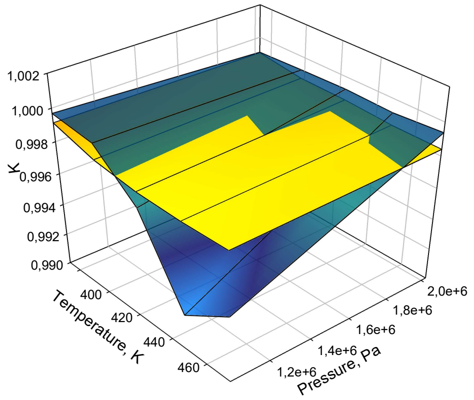

Figure 1. Equilibrium constant dependence on pressure and temperature in n-dodecane

The regions of the crossing of the obtained planes indicate the process conditions optimal for the chosen solvent. At these conditions, the stoichiometric ratio of the dissolved gases can be achieved.

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ANALYSIS OF THE NONEQUILIBRIUM STATE DIAGRAM IN THE DIPHENYL – DIBENZYL SYSTEM

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Pre–crystallization overcooling in the diphenyl - dibenzyl system has been studied by thermal analysis methods.

A nonequilibrium diagram of the diphenyl – dibenzyl state is constructed indicating metastable regions with overcooling under normal crystallization conditions (Figure).

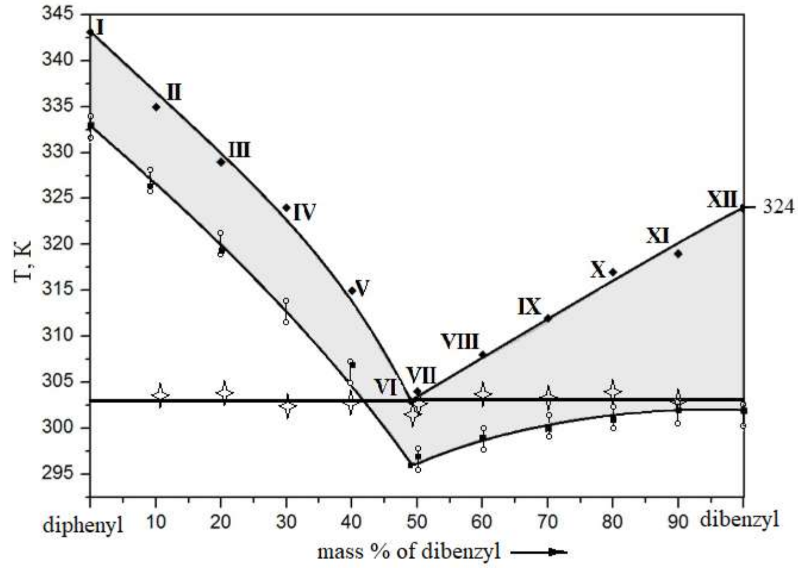

Figure. Diagram of the diphenyl – dibenzyl state with the lower boundaries of the metastable state.

Using the Schroeder equation for the liquidus line from both the diphenyl and dibenzyl sides, and solving these equations together, the eutectic coordinates ($x_E = 0.49$) and $T_E = 303.0$ K.

When analyzing the diagram, the following patterns were established. Firstly, with an increase in the concentration of the second component, overcooling naturally decreases in the pre–eutectic region from 10 degrees (for diphenyl), and in the post-eutectic region from 22 degrees (for dibenzyl) to ~ 7 degrees for the eutectic alloy (VI). Secondly, in general, the overcooling of pre-eutectic alloys was less than that of pre-eutectic alloys. Thirdly, in all samples, after appropriate overcooling to T_{min}, temperatures rose sharply at a rate of ~ 25-30 K/s from T_{min} to the corresponding liquidus temperatures T_L, which indicates the “explosive” nature of crystallization at the initial stage.

During the crystallization of pre–eutectic alloys in the diphenyl-dibenzyl system, diphenyl crystals with impurities in the form of dibenzyl $C_{14}H_{14}$ molecules are formed below the liquidus line, and in trans-eutectic alloys, on the contrary, during the formation of dibenzyl crystals, diphenyl $C_{12}H_{10}$ molecules are “impurities”. In both cases, an increase in the concentration of the second component contributes to heterogeneous crystallization, which, unlike homogeneous (for pure biphenyl and dibenzyl) occurs with less overcooling. This is confirmed by the decreasing metastability zone as the solutions shift to eutectic both on the left and on the right according to the diagram (Figure).

HEAT-RESISTANT EPOXY BINDERS WITH REDUCED FLAMMABILITY

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To control the properties and curing kinetics of epoxy oligomers, structural modification by adding compatible oligomers with higher functionality is widely used [1-2]. Such modifiers include promising representatives of polyfunctional epoxides – phosphazenes with epoxy groups in the organic radical, capable of interacting with reactive groups of the components of the epoxy composition. ED-20 epoxy resin was chosen as the main component of the binder, and epoxyphosphazenes, synthesized at the D. Mendeleev University of Chemical Technology of Russia, were chosen as the modifier [3-5]. Epoxyphosphazenes are an equilibrium mixture of diphenylolpropane diglycidyl ether and epoxyphosphazene diane epoxy oligomer. The aromatic diamine 4,4'-diaminodiphenylmethane was used as a hardener. The low viscosity of the resulting composition ensured the fluidity of the system under normal conditions. The curing mode is stepwise with a final curing temperature of 180°C. The inclusion of a three-dimensional network of phosphazene cycles in the composition of the thermosetting epoxy matrix formed during curing significantly changes the physical and mechanical characteristics of the cured system, and the presence of thermally stable phosphazene cycles in the network of chemical bonds affects the glass transition temperature of the binders. It has been established that modification of epoxy resin ED-20 with epoxyphosphazene oligomers leads to an increase in the glass transition temperature, mainly due to additional aromatic rings in the structure of the epoxyphosphazene resin, as well as due to the presence of nitrogen and phosphorus in the main ring. The glass transition temperature of the cured systems was studied by dynamic mechanical analysis using a DMA Gabo Eplexor instrument. For the unmodified binder based on ED-20, the glass transition temperature was 160 °C, for the system modified by epoxyphosphazene – 171 °C, and the cured phosphazene with epoxy groups had a glass transition temperature of 200 °C. The impact strength of the modified epoxy resin ED-20 passes through a maximum with increasing content of epoxyphosphazene modifier and is 3,9 kJ/m^2 for an unmodified binder based on ED-20, when 20 wt. including epoxyphosphazene modifier, impact strength increases to 10,2 kJ/m^2. It has been established that the formation of a dense three-dimensional network in the resulting modified binders does not lead to an increase in their fragility; it is likely that the areas of the chemical bond network formed by phosphazene components can be dissipators of impact energy, which leads to an increase in the resistance of the compositions to impact loads. It has been established that epoxy resin ED-20, modified with epoxyphosphazene, is characterized by reduced flammability and increased heat resistance. The resulting binders can be used to create materials with reduced flammability and low toxicity of combustion products in aerospace engineering. The modifiers used are effective flame retardants, which not only do not reduce the mechanical properties and thermal stability of epoxy binders, but also improve them due to the formation of a three-dimensional polymer network, in the nodes of which phosphazene rings are located.

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TA-ASSISTED KINETIC ANALYSIS OF SPINEL FORMATION IN VARIOUS CONDITIONS

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Spinels, which are one of the most important groups of modern inorganic functional materials, are widely used in various areas of material production. In this regard, it is understandable that there is an undiminished interest in them and a desire to comprehensively characterize their behavior. The study of the kinetics of spinel formation makes it possible to determine the optimal conditions for synthesis and predict the yield of the product.

An important characteristic is the activation energy, which is determined by both isothermal and non-isothermal methods. When choosing the latter, it is convenient to use thermal analysis (TA) data, namely differential scanning calorimetry [1] or thermomechanical analysis [2]. There are many models that allow for a more or less accurate determination of kinetic parameters, including the activation energy *of Ea*, using the TA data at different heating rates h and setting the maximum temperature of the corresponding thermal peak. Kissinger method, Augis and Bennett method, and Ozawa method are few of them which utilize, in one form or another, the linear relationship between different form of ln h and $1/T_{max}$ to determine the *Ea* of a reaction:

$$\ln\left(\frac{T_{max}^2}{h}\right) = \frac{E_a}{RT_{max}} + const \text{ (Kissinger equation);}$$

$$\ln\frac{h}{T_{max}} = -\frac{E_a}{RT_{max}} + const \text{ (Augis and Bennett equation);}$$

$$\ln h = -\frac{E_a}{RT_{max}} + const \text{ (Ozawa equation).}$$

In this work, the reaction of magnesia spinel formation was studied, based on various aluminum oxide precursors, including industrial corundum and alumina powders, as well as the combustion product of xerogel, obtained from aluminum nitrate and citric acid. The source of MgO was sintered periclase powder. Thermomechanical analysis (TMA) was performed, i.e., thermal expansion curves (dL/L_0) at different heating rates were taken and dependencies $d(dL/L_0)/dT - T$ were constructed. The last characterized by the presence of extreme points (maxima). With the h increase, the maxima shifted towards higher temperatures.

As in [2], the analysis of TMA curves obtained at different heating rates showed the possibility of using all three models (straight-line dependencies with a high linear approximation coefficient were obtained) and good convergence of the activation energy values. The use of a more active combustion product for the reaction of xerogel made it possible to reduce the value of *Ea*.

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The work was carried out within the framework of the state assignment for the implementation of research work (Topic No. FZZW-2024-0004).

DSC-BASED DETERMINATION OF EFFECTIVE ACTIVATION ENERGY OF MULLITE CRYSTALLIZATION

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Differential scanning calorimetry (DSC) is a convenient method for characterizing a number of solid-phase processes, in particular crystallization. It is widely used to describe the polymer hardening. In synthesis reactions, high-temperature complex oxide compounds are usually initially formed in an X-ray amorphous state and only then form a stable crystal lattice. Therefore, it is relevant for them to determine the crystallization activation energy using DSC.

The work determined the kinetic parameters for the crystallization of a mullite precursor obtained by coprecipitation from a solution of aluminum nitrate and sodium silicate pentahydrate with ammonia. After calcination at 900-1000 °C, the Al–Si spinel phase of γ-Al_2O_3 type was dominated, though some slight signs of crystalline mullite were already appeared. Sharp peaks which concerned to single orthorhombic mullite were registered since 1150-1200 °C; at the same time, the spinel reflexes practically disappeared. The most intensive phase changes were in the range of 1100-1200 °C. The effective activation energy *E*a has been calculated according to the Kissinger equation:

$$\ln\left(\frac{T_{max}^2}{h}\right) = \frac{E_a}{RT_{max}} + const,$$

where T_{max} – temperature of the exothermic peak which related to the mullite formation on the DSC curve, h – heating rate, *K/sec*, R – universal gas constant (8.314 J/(mol·K)).

For this purpose, DSC curves were obtained for mullite forming suspensions synthesized at pH 6.5 at various heating rates of samples [1]. Under heating rate increase the DSC curve deviation was shifted to the higher temperatures. The calculated value of the effective activation energy was (740 ± 40) kJ/mol. This magnitude was in a well accordance with the activation energy values for the diffusion of the Si^{4+} ions in the mullite layer which were estimated to range from 730 to 780 kJ/mol [2]. So, one might assume that the limiting stage was just the diffusion of the Si^{4+} ions.

The Johnson–Mehl–Avrami–Kolmogorov crystallization theory is expressed by the equation:

$$x = 1 - \exp\{-(Kt)^n\},$$

where x is the crystallized fraction, t is time, n is the Avrami exponent, and K is the rate constant.

The value of the Avrami exponent, n, was determined from the shape of the crystallization exotherm and was related to T_{max} by Augis and Benneth equation [3]:

$$n = \frac{2.5RT_{max}^2}{\Delta T E_a},$$

where ΔT is the width of a DSC crystallization peak at half maximum value.

The averaged value found for the Avrami exponent was 1.7±0.3 that suggested that the o-mullite crystallization was controlled by diffusion.

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The work was carried out within the framework of the state assignment for the implementation of research work (Topic No. FZZW-2024-0004).

THERMODYNAMIC PROPERTIES OF ETHYL-2-CYANO-3-(FURAN-2-YL)-PROP-2-ENOATE DERIVATIVES IN THE CRYSTAL AND GAS PHASES

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Thermodynamic properties of 2-cyano-3-[4-(4-methylphenyl)-2-furan] acrylic acid ethyl ester (I) and 2-cyano-3-[5-(2-nitrophenyl)-2-furan] acrylic acid ethyl ester (II) in condensed and ideal gas states were established. The samples of I and II were obtained in National University Lviv Polytechnic by methods described in [1] and [2] respectively.

The heat capacities at saturation pressure for I and II in the temperature range of (78 to 370) K were determined in an automatic vacuum adiabatic calorimeter TAU-10 (Termis, Moscow, Russia), described elsewhere [3]. Low temperature adiabatic calorimetry was used for sample I, heat capacities in the range of 5 to 80 K are represented at Figure 1. The standard thermodynamic functions of I and II in the condensed state were calculated using polynomial dependeces obtained from experimental data.

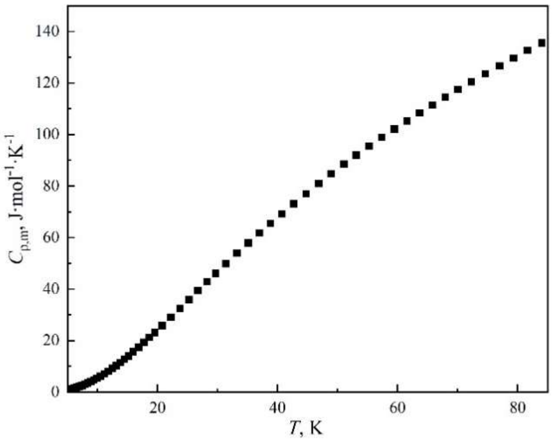

Figure 1. Heat capacity temperature dependence of the 2-cyano-3-[4-(4-methylphenyl)-2-furan] acrylic acid ethyl ester in the condensed state in the range of (5 to 80) K

The standard enthalpy of formation of the compound I was calculated using the composite quantum chemical method G3(MP2) and IDR approach. The standard thermodynamic functions of the derivatives of the 2-cyano-[2-furan] acrylic acid ethyl ester in the ideal gas state were obtained using statistical thermodynamics approach in the temperature range of (0 to 1000) K. The molecular and spectral data required for statistical thermodynamics calculations were determined at the B3LYP/6-311+G(3df,2p) theory level. The most stable conformations of compounds based on the potential-energy surface scans were established (DFT/B3LYP 6-311+G (3df,2p)).

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SOLVATION OF l-TRYPTOPHANE IN HIGHLY AQUEOUS WATER-TRET-BUTANOL MIXTURES: THE EVIDENCE OF ALCOHOL AGGREGATION

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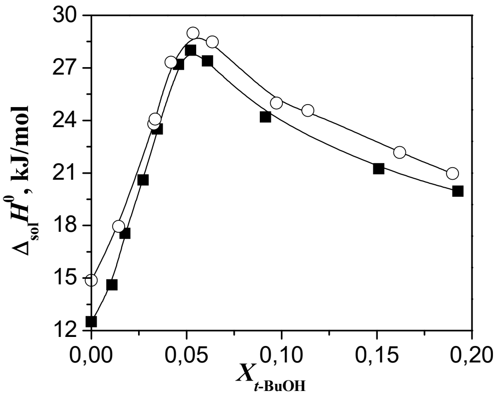
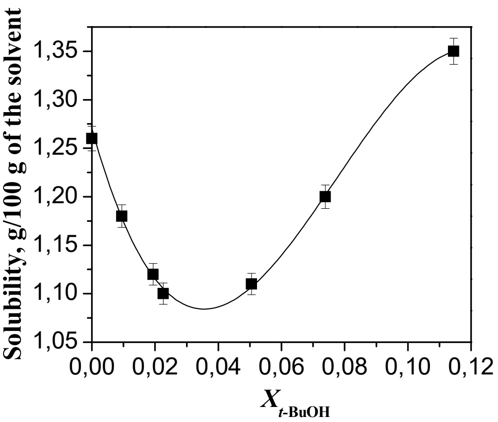
Large-scale MD simulations [1] indicate that *tert*-butanol (*t*-BuOH) molecules has a strong tendency towards aggregation in water and this aggregation enhances at elevated temperatures. The corresponding CH_3–CH_3 probability distribution functions obtained show that as the alcohol concentration increases much of waters in the first solute hydration shell are replaced by methyl groups confirming that the water loss coincides with solute aggregation induced by the *t*-BuOH- *t*-BuOH hydrophobic interaction. This alcohol self-association leads to the appearance of the pronounced maxima on the curves of the enthalpies of solvation of hydrophobic species in the water- *t*-BuOH mixtures at 298 K [2], for benzene the height of the extremum being comparable with the enthalpy of hydration. Here, we show that L-tryptophan containing a large hydrophobic fragment reveals a similar behavior both at the standard and elevated temperatures (see the left Figure below).





It is worthy of note that the amino acid solubility (see the right Figure) passes through a slight minimum in the region of cluster formation. It is obvious that the major source of this solute behavior is the hydrophobic indole residue which seems to be preferentially accumulated in alcohol clusters. The thermodynamic functions of L-tryptophan transfer from water to the mixed solvent, the amino acid-alcohol pair, triplet and high order interaction parameters [3] recovered from the experimental curves above as well as the fluorescence analysis of indole fragment solvation in the highly aqueous water- *t*-BuOH mixtures will be considered and discussed.

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THE EFFECT OF DOPING ON THE HEAT CAPACITY OF THE $LiNaGe_4O_9$ COMPOUND

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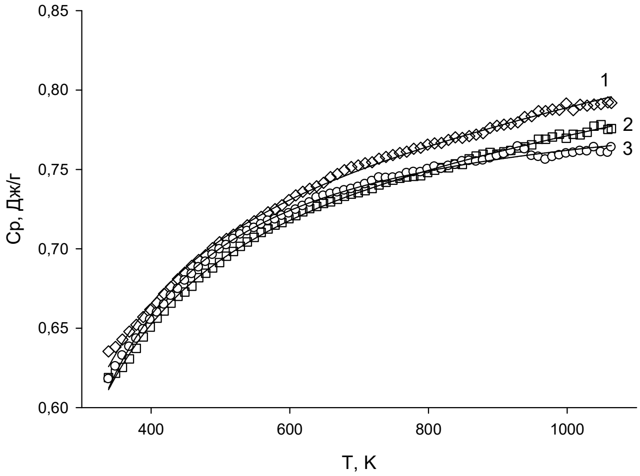
One of the phosphors emitting in the red and IR-ranges used in agriculture is the compound $LiNaGe_4O_9$ doped with the Mn(IV) ion [1]. There is information in the literature about the $LiNaGe_4O_9$ matrix doped with Mn(IV) ion, which indicates an insufficient quantum yield [2], and therefore it was decided to jointly dope $LiNaGe_4O_9$ with Mn(IV) and Al(III) ions.

In this work, three samples based on $LiNaGe_4O_9$ doped with Mn(IV) and Al(III) ions were synthesized: $LiNaGe_4O_9$; $LiNaGe_4O_9$:0.75Al^{3+};0.5Mn^{4+}; $LiNaGe_4O_9$:0.25Al^{3+};0.5Mn^{4+}.

The obtained samples were tested for single-phase using X-ray phase analysis on a VANTEC Bruker d8 Advance diffractometer (Germany). For practical use of phosphors, knowledge of their behavior during heating is often required: whether there is a phase transition, decomposition, temperature aging of the material, etc. You can track such changes by knowing the temperature dependence of the heat capacity of the compound. Figure 1 shows graphs of the dependence of heat capacity on temperature for the $LiNaGe_4O_9$ compound:xMn^{4+};yAl^{3+}.

The heat capacity of the compounds was measured by differential scanning calorimetry using a Jupiter NETZSCH STA 449 C thermal analyzer (Germany). The error in measuring the heat capacity does not exceed 2.5%.



1 - $LiNaGe_4O_9$:0.75Al^{3+};0.5Mn^{4+}; 2 - $LiNaGe_4O_9$:0.25Al^{3+};0.5Mn^{4+}; 3 - $LiNaGe_4O_9$
Figure 1 – Dependence of the heat capacity on the concentration of Al^{3+}

It can be seen from the graph that an increase in the aluminum content in the compound practically does not affect the dependence of the heat capacity on temperature. There are no changes in the entire temperature range of the measured heat capacity, which allows us to speak about the thermal stability of these samples with increasing temperature.

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CONTROL OF SELF-ASSEMBLY OF NANOPARTICLES CHANGES IN THE COMPOSITION OF A HETEROGENEOUS LIQUID SYSTEM

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Effective control of the self-assembly of nanoparticles at the interface of two immiscible liquids is important due to the possibility of obtaining new unique materials. The interface of immiscible liquids has increased energy, which will be reduced when a monolayer of particles appears on it, and the particles must be located precisely on the interface. The decrease in interfacial energy associated with the displacement of particles into the liquid volume is determined by the particle size, contact angle and interfacial tension [1]. These values are closely related to the composition of the system. Therefore, by changing the composition of the system, it is possible to control the process of self-assembly of particles at the liquid-liquid interface.

The purpose of the work is to assess the influence of the composition of a system of two immiscible liquids containing reagents, during the chemical interaction of which new molecules are formed that can be retained on the interface. Since the ultimate goal of our research is to obtain superhydrophobic materials, we chose the contact angle of the material of interfacial formation (MIF) transferred to a solid support as an indirect indicator characterizing the self-assembly of particles on the interface.

The interaction of aqueous solutions of chlorides of *d*- or *f*-elements with organic acid (stearic, myristic, di-(2-ethylhexyl)phosphoric) dissolved in a non-aqueous solvent (hexane, heptane, decane, toluene, carbon tetrachloride) was studied. The organic acid salt molecules that arise as a result of the reaction are adsorbed on the interface and, as a result of self-assembly, form nanoparticles. By varying the concentration of organic acid, it is possible to influence the self-assembly process to a certain extent. Over time, nanoparticles form larger aggregates; structure formation is observed. The MIF formed at the interface of two immiscible liquids has good adhesive ability and can be easily transferred to a substrate using a method similar to the Langmuir-Blodgett method, used when removing condensed films from the liquid-air interface. The MIF interfacial material synthesized in the interfacial layer has controlled wettability. With increasing time of interfacial synthesis, the taken material acquires more hydrophobic properties. In the series of acids studied, it was possible to obtain coatings with a contact angle of 98° for myristates, 110° for stearates, and 135° for di-(2-ethylhexyl) phosphates. Higher contact angle values are observed for coatings based on salts of *f*-elements, and in the series of solvents studied, for alkanes.

Thus, the interface of two immiscible liquids, each of which contains a reagent that is insoluble in the adjacent liquid, but as a result of a heterophase reaction between them, molecules of a substance are formed that are capable of adsorption and self-assembly of nanoparticles, then larger aggregates, is a convenient place for obtaining materials with new properties.

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CALCULATION OF BISMUTH(III) BROMIDE MONO(IMINO)ACEANTHRENONE COMPLEXES

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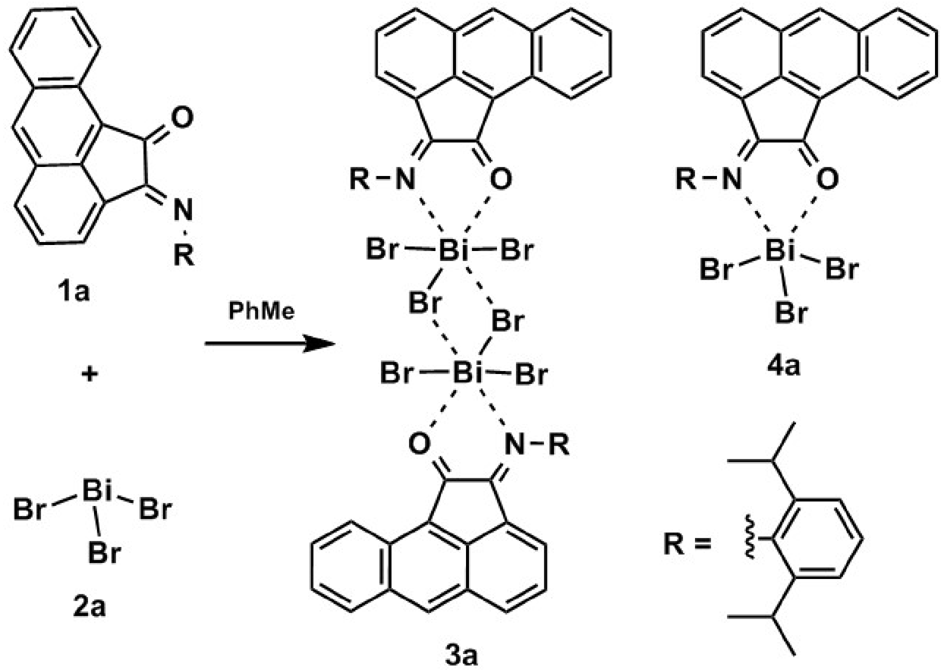
(E)-2-(2,6-diisopropylphenylimino)aceanthrylen-1(2H)-one (**1a**) reacts with bismuth(III) bromide (**2a**) in toluene at 423 K (in a sealed degassed ampoule) to form dark red crystals. According to X-ray diffraction data, coordination complex bis((2-(2,6-diisopropylphenylimino)aceanthrylen-1(2H)-one)bismuth(III) bromide) (**3a**) is formed, which has a dimeric structure. In order to estimate the energy of the coordination bond of iminoketone **1a** with bismuth(III) bromide and the energy of dimerization, a quantum chemical calculation of the **1a** molecule, **2a**, dimer **3a** and monomer (2-(2,6-diisopropylphenylimino)aceanthrylen-1(2H)-one)bismuth(III) bromide (**4a**) was performed. Based on the data obtained, the energy of the coordination bond iminoketone **1a** with bismuth(III) bromide and the energy of dimerization were calculated. These values were 9 and 36 kcal/mol, respectively. Thus, the driving force for the formation of coordination complex **3a** is mainly the energy of dimerization by bismuth fragments.



The work was supported RSF (№ 23-23-00474) and carried out use "Analytical Center of the IOMC RAS", "Ensuring the development of the material and technical infrastructure of the centers for collective use of scientific equipment "(RF----2296.61321X0017, N 075-15-2021-670).

THERMODYNAMIC BARRIER TO THE FORMATION OF A CRITICAL-SIZED CRYSTALLINE EMBRYO IN SILICATE GLASSES

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The crystallization of supercooled glass-forming melts is a phase transition of the first kind. To characterize the phase at constant temperature T and pressure p, Gibbs free energy, G. In order to indirectly estimate the experimental data the Zeldovich equation was used [1]. Nuclei (precursors, precursors of crystallization) are present in the glass melt. Subcritical embryos, whose radius is less than the critical one ($r<r^*$), tend to spontaneously disappear (dissolve). Embryos whose size exceeds the critical size are stable and capable of further growth, since their growth is accompanied by a decrease in the free energy of the system [2, 3]. The frequency of formation of such nuclei determines the rate of nucleation. On the way to the formation of a stable crystalline embryo, there is a thermodynamic barrier that the embryo needs to overcome in order for the nucleation to be realized. A measure of the magnitude of this barrier can be the work to create the surface of the embryo, W^*, which is determined from the obtained values of the surface energy σ and the size of the critical embryo r^* for different temperatures of pre–heat treatment of glasses in the temperature range (420 - 490 °C) and their further development at 600 °C. In turn, σ and r^* are obtained from the experimentally found fundamental characteristics of crystal nucleation in the studied glasses: the rate of stationary crystal nucleation I_{st}, the time of unsteady crystal nucleation, τ, the measure of which is the time of the induction period t_{ind}, and the difference in the specific free energies of glass and crystal, $\Delta\varphi$. Calculated values of the surface energy σ at the crystal nucleus-glass interface, size of crystal nucleus r^*, and the work to create the surface of the embryo, W^* are presented at the table.

T,°C	σ, эрг/см^2	r^*, Å	$W^*\cdot10^{13}$, эрг
420	84.00	8.91	27.92
440	85.60	9.33	31.18
460	86.00	9.66	33.60
480	87.90	10.14	37.80
490	90.40	10.60	42.48

The sizes of critical nuclei of crystals of lithium and sodium di- and metasilicates nucleated in glasses of lithium and sodium silicate systems are determined. A comparison of the sizes of critical nuclei with the sizes of elementary cells of lithium and sodium di- and metasilicate allows us to conclude that in order for crystal nucleation to occur on a critical embryo, it is sufficient that the size of the critical embryo is equal to one or two elementary cells. The values of W* in these glasses varied within the values shown in the table from 27.92 to 42.48 erg.

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EFFECTS OF CONCENTRATING AND MICROENVIRONMENT IN MICELLAR CATALYSIS OF PERHYDROLYSIS OF MODEL ECOTOXICANTS

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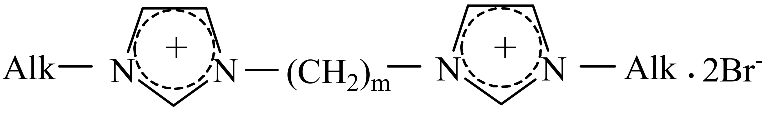
There is a need in a safe and inexpensive solvent for destruction of highly toxic chemicals, including phosphororganic compounds (POCs). Water looks as the most appropriate for this purpose, but POCs (similarly to other model analogs of ecotoxicants) are practically insoluble in water. Organized microheterogeneous systems (OMS) based on cationic surfactants are usually in use as reaction media. In these OMS reagents are distributed between micellar pseudophase and water volume as a result of electrostatic and hydrophobic interactions. Among new synthetic surfactants, dicationics(gemini surfactants, GS) are of specific interest as host molecules due to unique physicochemical properties, such as extremely low cmc, highly effective sorption, and so on. As a nucleophilic reagents α-nucleophiles are preferential, in particular HOO^{-}anion that readily destroys POCsin at slightly alkaline water medium.

Kinetics of perhydrolysis of 4-nitrophenyldiethylphosphonate was studied in OMS based on imidazoliumdicationic GS (I) and monocationic (II) surfactants.



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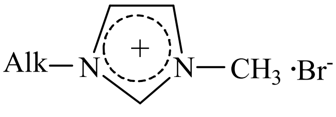

II

Alk = $C_{16}H_{33}$, $C_{14}H_{29}$, $C_{12}H_{25}$, m = 2, 3, 4 Alk = $C_{16}H_{33}$,$C_{14}H_{29}$, $C_{12}H_{25}$

Experimental results were analyzed with pseudophase distribution model. In a frame of this model, the next parameters were used to evaluatephysicochemicalcharacteristics of perhydrolysis:

1. The ratio of observed rate constants in water ($k^{w}_{obs.}$, s^{-1}) and micelles ($k^{m}_{obs.}$, s^{-1}). The value of $k^{m}_{obs.}/k^{w}_{obs.}$ represents micellar effects and can reach 10^2.
2. The ratio of second order rate constants(k_2^{w} и k_2^{m}, $M^{-1}\cdot s^{-1}$).The value of k_2^{m}/k_2^{w} makes possible to evaluate the role of microenvironment in micellar effects of OMS. Nucleophilicity of HOO^{-}-anion do not change in micelles, and do not exceeds 2-3-fold reactivity of HO^{-}-anion.
3. The partition coefficients (K_s, M^{-1}) mirrored an effectiveness of reagents solubilization, the substrate first of all. The value of K_s depends on structures of substrate and surfactant; hydrophobic interactions play a key role. Concentrating is the most significant part of micellar effect, increasing an overall reaction rate up to 50-fold.

In conclusion, dicationic surfactants make possible to achieve the same rates of POCs destruction at concentrations an order of magnitude lower than for monocationics. So, OMS based on GS are highly effective in perhydrolysis of model ecotoxicants, and may serve as a basis for decontaminating recipes.

HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS NEW TITANIUM-MANGANITE LANTHANUM AND BARIUM $LaBaTiMnO_6$

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It is known that substituted manganites of rare-earth and alkaline earth metals have unique physical and chemical properties [1].

Titanium-manganite $LaBaTiMnO_6$ was obtained by the method of high-temperature interaction of lanthanum (III) oxides of the "os.ch.", titanium (IV), manganese (III) and barium carbonate of the "c.d.a." grade. It has been established that this titanium-manganite crystallizes in cubic syngonium with lattice parameters: a = 13.82±0.02 Å; V^o=2642.67±0.07 Å^3; Z=4; $V^o_{el.cell}$=660.67±0.02 Å^3; $\rho_{roent.}$=4.55 g/cm3; $\rho_{pick.}$=4.54±0.01 g/cm^3 [2].

The heat capacity of the synthesized $LaBaTiMnO_6$ was studied in the range of 298.15-673 K using the IT-S-400 dynamic calorimeter.

It has been established that there $C^o_p \sim f(T)$ is an anomalous peak on the curve of the compound at 348 K, probably associated with a phase transition of the II-kind. On the basis of experimental data, taking into account the temperature of the phase transition, the equations of the temperature dependence of heat capacity [J/(mol K)] were derived:

$$C^o_{p(I)} = -(7.5 \pm 0.4) + (780.2 \pm 45.4)\cdot 10^{-3}T, \qquad (298.15\text{-}348\ K), \qquad (1)$$

$$C^o_{p(II)} = (1060 \pm 62) - (2287.5 \pm 133.1)\cdot 10^{-3}T, \qquad (348\text{-}398\ K), \qquad (2)$$

$$C^o_{p(III)} = (843 \pm 49) - (301.2 \pm 17.5)\cdot 10^{-3}T - (908.6 \pm 52.9)\cdot 10^{5}T^{-2}, \ (398\text{-}673\ K). \qquad (3)$$

The standard entropy of the compound was calculated using ionic entropy increments according to [3]. The temperature dependencies of $C^o_p(T)$ and the thermodynamic functions $S^o(T)$, $H^o(T) - H^o$ (298.15 К) and $\Phi^{xx}(T)$ were calculated.

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DFT STUDY OF PHENOXY BASED ZIRCONIUM/METYLALUMINOXANE COMPLEXES AS CATALYSTS TOWARDS THE POLYMERIZATION OF ETHYLENE

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Polyolefins such as polyethylene and polypropylene are the most widely used polymers in the world. More than 60 million tons of polyolefins are produced every year using catalytic processes based on transition metals. Although multicenter Ziegler-Natta catalysts have been the "workhorses" of the polyolefin industry for many years, recently the presence of single-center "single-site" catalysts, represented by metallocene catalysts and non-metallocene catalysts with stable geometry ("constrained-geometry catalysts), has been noticeably increasing in the global polyolefin market.

On the other hand, in the last few decades, significant advances have occured in computational modelling towards understanding the nature of active sites and key reaction steps. It is known that ligands in metal complexes play an important role in the formation of catalytic active centers in organometallic catalysis. The nature of catalytic centers is also known to have a great influence on the preparation of (co)poymers with various structures [1]. For this reason, ligand selection is a very important factor to obtain products with desired properties.

The DFT study of ionic-liquid ligands (such as [bmim]BF4 and [bmim]HSO4) and arilimine metal complexes was performed through the calculations for geometry optimization, activation energy, dipol moment, bond angles and bond length. Frontier orbitals and chemical reactivity of the ligands and their metal complexes was described through the HOMO and LUMO orbital calculations. The HOMO and LUMO orbitals are commonly known as Frontier Orbitals and were found extremely useful in explaining chemical reactivity.

These catalytic systems using organoaluminium compounds such as methylaluminiumoxane and (C2H5)2AlCl provide the formation of linear PE mixtures with high density, different thermodynamic properties, molecular mass distribution and cristallinity. It has been found that these catalytic systems allow to control the structure and composition of the products obtained. It was found that 4-methyl salisylic aldlehyde +2,6-dimethylaniline based ligand gives metal complex a higher polarity and less stability. Whereas salisylic aldehyde +aniline based ligand gives metal complex less polarity and high stability. The solubility of these complexes in ionic liquids during the polymerization of ethylene leads to obtain similar activity under the same conditions and production of high - density polyethylene in the presence of both catalytic systems. However, the molecular mass distribution in the presence of these catalytic systems are different. The molecular mass distribution is narrower in the presence of 4-methyl salisylic aldlehyde +2,6-dimethylaniline based ligand, whereas broader molecule weight values are obtained in the presence of salisylic aldehyde +aniline based ligand.

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APPLICATION OF POLYMOLECULAR ADSORPTION MODEL TO DESCRIBE THE BEHAVIOR OF MODIFIED HUMIC ACIDS SALTS IN THE SURFACE LAYER

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Humic acids (HA) are natural polyelectrolytes that have a variety of beneficial properties that can be enhanced by their modification. In this work were studied salts solutions of modified HAs obtained by solid-phase mechanochemical synthesis: sodium salts of ethoxyhumic (SH$_{\text{HA + PEG-6000}}$ and SH$_{\text{HA + PEG-1500}}$), aminohumic (SH$_{\text{HA + cyanoguanidine}}$) and ethoxyaminohumic (SH$_{\text{HA + PEG-6000 + cyanoguanidine}}$ and SH$_{\text{HA + PEG-1500 + cyanoguanidine}}$) acids.

The expressions of a theoretical model of polymolecular adsorption, developed to characterize the adsorption properties of protein solutions as natural polyelectrolytes, were used for a semiempirical description of experimental results obtained for HA salts solutions [1, 2]. The model considers the possibility of the macromolecules existence in **n** states and their ability to aggregate in adsorption layers during polymolecular adsorption. The model includes the following characteristics: $\boldsymbol{\omega_0}$ – molar area per one macromolecule segment in the first adsorption layer (molar area increment), $\boldsymbol{\omega_{min}}$ – minimum molar area in the first adsorption layer, $\boldsymbol{\omega_{max}}$ – maximum molar area in this layer. The calculated values of the adsorption model parameters for HA salts are given in the table; $\overline{M}$ – average molecular weight measured by viscometric method.

Ratio $\omega_{max} / \omega_{min}$ for the sample SH$_{\text{HA + PEG-6000 + cyanoguanidine}}$ is close to the value characteristic for β-casein ($\omega_{max}/\omega_{min} = 10$), protein well known for its high structural flexibility [1]. For other HA samples, these values are close to globular proteins (β-lactoglobulin, $\omega_{max}/\omega_{min} \approx 2$). Number of possible states **n** that macromolecules of SH$_{\text{HA + PEG-6000 + cyanoguanidine}}$ may take on in the surface layer is greater than for other HA samples, which may be caused due to the larger value $\overline{M}$ through the incorporation of long ethoxylated fragments into the structure of their macromolecules as a result of the solid-phase reaction with PEG-6000.

Table. Parameters of the polymolecular adsorption model of polyelectrolytes for HA sodium salts (Program ProteinG [2]).

Sample	$\omega_0 \cdot 10^5$, m^2/mol	$\omega_{min} \cdot 10^6$, m^2/mol	$\omega_{max} \cdot 10^7$, m^2/mol	$\omega_{max}/\omega_{min}$	n	$\overline{M}$
SH [1]	3,00	2,50	1,00	4,00	26	14000
SH$_{\text{HA + PEG-6000}}$ [1]	5,00	4,00	1,00	2,50	13	15500
SH$_{\text{HA + PEG-1500}}$	5,63	4,75	2,00	4,21	9	14870
SH$_{\text{HA + cyanoguanidine}}$	5,43	5,44	1,01	1,86	9	14000
SH$_{\text{HA + PEG-6000 + cyanoguanidine}}$	5,91	4,89	4,00	8,17	60	26000
SH$_{\text{HA + PEG-1500 + cyanoguanidine}}$	5,45	7,79	1,38	1,87	10	16300

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THERMODYNAMIC STUDY OF THE Mn(Sn)-Bi-Te SYSTEMS

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The discovery of a topological insulator (Tl) - a new quantum state of matter [1] served as an impetus for the study of tetradymite-like layered materials, in particular ternary compounds formed in quasi-binary systems $ATe\cdot B_2Te_3$ (A – Mn, Ge, Sn, Pb; B-Sb, Bi). They have been shown to be three-dimensional topological insulators and are extremely promising for use in spintronics, quantum computing, as well as scanning devices in medicine, security systems, etc. [2].

To develop methods and optimize conditions for the directed synthesis of new complex phases, the reliable data on phase equilibria and thermodynamic properties of the corresponding systems are require.

The aim of this work is the studying phase equilibria in the Mn(Sn)Te-Bi_2Te_3-Te systems and the thermodynamic properties of ternary phases using electromotive forces (EMF) method.

Alloys of the both system were prepared using pre-synthesized starting binary MnTe, SnTe and Bi_2Te_3 compounds and elemental tellurium. All alloys were synthesized at 1000 K for 5 h followed by quenching in icy water. The resulting ingots were annealed at 700 K for 45 days and 400 K for 5 days to form equilibrium phases, and examined using differential thermal analysis (LINSEIS HDSC PT1600 system) and X-ray diffraction (Bruker D2 PHASER diffractometer) techniques. EMF measurements were performed using a Keithley 2100 6 1/2 Digit Multimeter.

According to phase diagrams, the MnTe-Bi_2Te_3 system [3] is characterized by the formation of the $MnBi_2Te_4$, $MnBi_4Te_7$, $MnBi_6Te_{10}$, $MnBi_8Te_{13}$ ternary compounds, and in the SnTe-Bi_2Te_3 system $Sn_3Bi_2Te_6$, $Sn_2Bi_2Te_5$, $SnBi_2Te_4$, $SnBi_4Te_7$, and $SnBi_6Te_{10}$ compounds are formed [4]. According to XRD results, it is revealed that in the first system, all the ternary compounds and β-phase based on Bi_2Te_3 have a tie-line connection with $MnTe_2$. In second system, all the tin –bismuth tellurides, as well as solid solutions based on SnTe (α) and Bi_2Te_3 (β) form tie-line with elementary tellurium.

In order to study thermodynamic properties of ternary phases, the concentration cells of

$$(-)\ \text{ATe (solid)}\ |\ \text{liquid electrolyte, } A^{2+}\ |\ \text{(A–Bi–Te) (solid)}\ (+) \qquad (1)$$

types were assembled and their EMF were measured in the 300-450 K temperature interval.

The relative partial thermodynamic functions of MnTe and SnTe in various phase regions of the studied systems were calculated from the EMF data of (1) -type concentration cells. These data together with the corresponding thermodynamic functions of MnTe, SnTe and Bi_2Te_3 were used to calculate the relative partial molar functions of manganese and tin in alloys, and also the standard thermodynamic functions of formation and standard entropies of the above listed ternary compounds, and solid solutions based on initial binary compounds.

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THERMODYNAMIC PROPERTIES OF THE IRON-GALLIUM SULPHIDES

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Compounds of the MB_2X_4 type (M – Mn, Fe; B – Ga, In,; X – S, Se, Te) are promising functional materials possess thermoelectric, magnetic and optical properties, which makes them very promising for production of wide-gap converters of optical radiations, optical modulators, and other magnetic field controllable functional devices. These compounds have attracted the attention also because of their promise for spintronics [1-3]

The development of methods for directed synthesis of these phases is based on data on phase relations and thermodynamic properties of the corresponding systems [4].

The purpose of this work was to study solid-phase equilibria and thermodynamic properties of Fe-Ga-S system by measuring the electromotive forces (EMF) of the following concentration cells

$$(-)\ \mathrm{Fe\ (s.)}\ |\ \mathrm{glycerol + KCl + FeCl_3}\ |\ \mathrm{(Fe\ in\ alloys)\ (s.)}\ \ (+) \qquad (1)$$

$$(-)\ \mathrm{FeX\ (s.)}\ |\ \mathrm{glycerol + KCl + FeCl_3}\ |\ \mathrm{(Fe\ in\ alloys\ )\ (s.)}\ \ (+) \qquad (2)$$

in the 300-380 K temperature range.

Cells of type (1) were used to determine the partial molar functions of Fe in monochalcogenide, and cells of type (2) were used to determine the partial properties of FeX in alloys richer in chalcogen.

Alloys – anodes of the cells of type (1) and (2) were synthesized in 2 stages. First, using high purity iron (99.995%), gallium (99.999%) and sulfur (99.99%) purchased from Alfa Aesar as starting materials, compounds FeS and Ga_2S_3 were synthesized and identified. Syntheses were carried out in evacuated quartz ampoules in two-zone mode. Then, by fusing the above synthesized compounds in calculated ratios with the addition of 1-2 at% excess sulfur, also in vacuum conditions, alloys from the $FeGa_2S_4$-Ga_2S_3-S and $Fe_2Ga_2S_5$-$FeGa_2S_4$- S three phase regions were obtained. To achieve a state closest to equilibrium, the samples were subjected to stepwise thermal annealing (200 hours at 1000 K, 300 hours at 700 K and 100 hours at 380 K).

Powder X-ray diffraction analysis was used to control the achievement of equilibrium and the phase compositions of the alloys.

By combining the experimental data of the obtained concentration cells of types (1) and (2), the partial thermodynamic functions of Fe in the alloys are determined, based on which the standard thermodynamic formation functions and the standard entropies of the $FeGa_2S_4$ and $Fe_2Ga_2S_5$ intermediate compounds are calculated.

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THE EFFECT OF NaCl CONCENTRATION ON THE SURFACE-ACTIVE PROPERTIES OF SALTS OF ETHOXYAMINOHUMIC ACIDS

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Humic acids (HA) are natural anionic polyelectrolytes that have pronounced surfactant (surfactant) properties. The unique structure and functional diversity of HA in combination with biocompatibility, environmental safety and the possibility of directed chemical modification open new prospects for the application of HA derivatives in medicine, bioengineering and technical areas [1, 2].

The interaction between ionic surfactants and electrolytes has attracted particular attention in the optimisation of technological processes involving water-salt solutions. In this work, the influence of NaCl concentration on the surface-active properties of solutions of the sodium salt of ethoxyaminohumic acid obtained by mechanochemical synthesis through the interaction of humic acid with polyethylene glycol (PEG-6000) and urea was investigated.

The addition of NaCl to the solution of ethoxyaminohumic acid salt (figure) leads to a decrease in the equilibrium surface tension (γ_E) and an increase in the dilatational modulus of viscoelasticity (|E|). The increase in NaCl concentration favours a decrease in the electrostatic component of the adsorption barrier and allows an additional amount of surfactant to reach the surface [3], which is the reason for the decrease in surface tension and the increase in |E|.

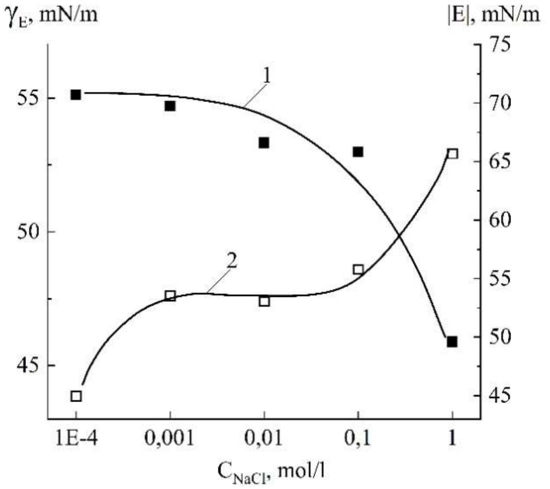

Figure. The effect of NaCl concentration on the surface characteristics of sodium ethoxyaminohumate solutions: 1 - $\gamma_P = f(C_{NaCl})$, 2 - $|E| = f(C_{NaCl})$, $C_{surfactants} = 0.1$ %. Tensiometer PAT-2P (SINTERFACE Technologies, Germany).

Thus, the sodium salt of ethoxyaminohumic acid, which has the functions of an anionic, cationic and non-ionogenic surfactants shows pronounced surfactant properties at high concentrations of NaCl, up to 1.0 mol/l.

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NANOPARTICLE SIZE EFFECT ON THERMAL STABILITY AND HEAT RESISTANCE PARAMETERS OF NANOCOMPOSITE OF Bi_2Te_3 NANOPHASE AND ARABINOGALACTAN

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The necessity of heat resistance evaluation of functional nanomaterials is directly related to their application. The heat resistance of materials determines their operating temperature range. Synthesis and research of promising structure-components for the development on their basis of materials demanded in technical applications that retain structural integrity, and hence their properties, is an actual direction. Thus, in accordance with the current trends in the search for high ZT polymer nanocomposite thermoelectrics [1, 2], we proposed the synthesis of composites consisting of Bi_2Te_3 nanoparticles stabilized by a polymer matrix of arabinogalactan (AG). For the obtained AG-Bi_2Te_3 polymer nanocomposite thermoelectrics containing 3.6 and 10.0 wt % of inorganic phase and average particle size of 33.6 and 71.0 nm, respectively, the thermal properties have been investigated and the main regularities of their thermoactivity changes have been determined, primarily due to the introduction of Bi_2Te_3 nanoparticles into the AG polymer matrix.

The results of simultaneous thermal analysis of AG matrix and nanocomposites, performed using NETZSCH Jupiter STA449F1 [3] and heating rate of 10 °C/min (Table 1) showed that the thermal degradation of AG proceeds in two stages associated with the evaporation of adsorbed water and the thermal decomposition of AG itself. The thermal decomposition of AG-Bi_2Te_3 nanocomposites is characterized by the presence of three main stages and a shift of the main decomposition stage to the low temperature region. The AG-Bi_2Te_3 decomposition stage following the first stage is characterized by the occurrence of a number of processes associated with both intramolecular dehydration of AG macromolecules and its oxidation and decomposition, which is clearly reflected in the mass spectra of thermolysis products of nanocomposites. Due to the above, the presence of Bi_2Te_3 nanoparticles in the matrix leads to a lower heat resistance compared to the data for the matrix. Some basic parameters of thermal stability of the investigated samples are presented in Table 1.

Table 1. Thermal stability and heat resistance parameters of the samples

Sample	$T_{onset\ II}$, K	$T_{main\ peak}$, K	T_5, K	T_{10}, K	T_{30}, K	T_{50}, K	T_{HRI}, K
AG	513.0	583.0	361.2	547.9	575.3	583.1	379.0
AG-Bi_2Te_3 (3.6 wt%)	477.0	574.0	363.4	475.9	564.6	582.9	376.5
AG-Bi_2Te_3 (10.0 wt%)	479.0	583.0	378.9	523.7	571.4	584.2	381.6

It should be noted that an increase in the mean size of nanoparticles leads to a shift of the second and third stages of the thermal destruction in the region of high temperatures, confirming the dependence of the thermal activity of composites on the size characteristics of the nanophase included in their composition.

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MODELING OF CHEMICAL INTERACTION IN THREE-COMPONENT SYSTEMS

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The construction of phase trees of the three-component oxide systems CaO–MgO–SiO_2, CaO-Al_2O_3-SiO_2 and the chloride system KCl–$CaCl_2$–$BaCl_2$ is presented. The phase tree of CaO–MgO–SiO_2 system includes three cycles represented by fifteen simplexes. The stable complex of the CaO-Al_2O_3-SiO_2 system contains fifteen secondary phase triangles. The phase tree of KCl–$CaCl_2$–$BaCl_2$ system includes four secondary phase triangles.

The initial stage of describing a chemical interaction is the drawing of unstable secants. Unstable secants at the intersection with stable secants form equivalence points. For mixtures that meet equivalence points, the chemical interaction is described in accordance with the law of equivalents. The possibility of the occurrence of basic chemical reactions is confirmed by thermodynamic calculations of thermal effects and Gibbs energies for standard conditions.

In addition to the main reactions for mixtures at equivalence points, phase trees make it possible to describe chemical interactions in the given systems using the method of atomic and ionic balance. In oxide systems, the formation of binary and ternary compounds of congruent and incongruent melting was noted. The formation of binary compounds was observed in the chloride system. As an example, the following reaction equations involving some of the compounds can be given.

$Ca_3Al_2O_6 + 4SiO_2 = 2CaSiO_3 + CaAl_2Si_2O_8$
($\Delta_f H^\circ_{298} = -282.5$ kJ; $\Delta_f G^\circ_{298} = -278.9$ kJ)

$Ca_3SiO_5 + CaAl_2Si_2O_8 = 2CaSiO_3 + Ca_2Al_2SiO_7$
($\Delta_f H^\circ_{298} = -104.5$ kJ; $\Delta_f G^\circ_{298} = -105.4$ kJ)

$CaBaCl_4 + KCl = KCaCl_3 + BaCl_2$
($\Delta_f H^\circ_{298} = -15.03$ kJ; $\Delta_f G^\circ_{298} = -16.66$ kJ)

$2CaBaCl_4 + K_2BaCl_4 = 2KCaCl_3 + 3BaCl_2$
($\Delta_f H^\circ_{298} = -36.61$ kJ; $\Delta_f G^\circ_{298} = -25.12$ kJ)

$2KCaCl_3 + 3K_2BaCl_4 + 4CaBaCl_4 = 6KCaCl_3 + K_2BaCl_4 + 6BaCl_2$
($\Delta_f H^\circ_{298} = -73.23$ kJ; $\Delta_f G^\circ_{298} = -50.24$ kJ)

It is concluded that for all mixtures corresponding to equivalence points, interactions are thermodynamically possible under standard conditions. Based on phase trees, taking into account data on faceting elements, a forecast of crystallizing phases in stable secants and in phase secondary triangles was made.

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SATURATED VAPOR PRESSURE OF 2,2-DIMETHYLBUTYRIC ACID ESTERS AND C_1-C_{10} ALCOHOLS OF LINEAR STRUCTURE

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Ester products are widely used in various industries: they are used as plasticizing compositions, lubricants, selective extractants for petrochemicals, as well as green solvents. [1]

Various alcohols and carboxylic acids are utilized to impart a variety of physicochemical and operational characteristics to materials during the synthesis of compounds within this class. From the entire variety of saturated carboxylic acids 2,2-dimethylbutyric acid stands out the most. Carboxylic acids that have a structure similar to that of 2,2-dimethylbutyric acid can be used as selective extractants for rare metals.

No information is available on the esters of 2,2-dimethylbutanoate, with the exception of boiling point data for methyl and ethyl esters.

In order to recommend the use of 2,2-dimethylbutyric acid esters, it is essential to evaluate their physicochemical characteristics. One of these characteristics is data on liquid-vapor equilibrium and enthalpy of vaporization, which can help determine the temperature limits for their use.

In this study, esters of 2,2-dimethylbutyric acid and linear alcohols C_1-C_{10} were synthesized. The synthesis was carried out in a mixing reactor equipped with a Dean-Stark apparatus, a magnetic mixer. In order to shift the equilibrium towards the formation of desired products, a carboxylic acid – alcohol ratio of 1:6 was employed, respectively. The catalyst is sulfuric acid. Purification was carried out by distilling excess alcohol with further separation of the target compound by column chromatography. The resulting compounds were >99.5% pure by weight.

The saturated vapor pressure values were estimated by the transfer method according to the method described in [2]. The saturated vapor pressure values were processed by a 3-parameter equation:

$$R \cdot ln\, p_i = a + \frac{b}{T} + \Delta_l^g C_p \cdot ln\left[\frac{T}{T_0}\right]$$

Based on the obtained values of the saturated vapor pressure, the enthalpy of evaporation was estimated, after which the enthalpy was brought to a temperature of 298.2 K. The QSPR method was used to estimate the evaporation heat capacity required to calculate the enthalpy. [3]

The obtained values of the enthalpy of evaporation were compared with the values of the enthalpy of evaporation obtained by gas chromatography. The obtained values are in satisfactory agreement.

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SELF-ORGANISATION OF COMPLEX CHEMICAL SYSTEMS. OXIDATION OF HYDROCARBONS IN MICROHETEROGENEOUS SYSTEMS BY ADDITIVES OF SURFACTANTS

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The scientific basis for oxidation process control is the theory of liquid-phase oxidation developed for homogeneous and heterogeneous systems. At the same time, many real systems are microheterogeneous, aqueous-organic or become so in the process of operation [1]. As initiators of microaggregation the most known and the least reactive in radical-chain oxidation processes sodium alkyl sulfate (DDS) and cetyltrimethylammonium bromide, including saturated hydrocarbon fragments in the composition of the molecule, were used .Regularities of oxidation of hydrocarbons (dodecane, ethylbenzene, cumene) (RH) and decomposition of hydroperoxides in microheterogeneous systems formed at additions of surfactants and solid microdisperse systems in hydrocarbon medium were investigated.A pronounced influence of surfactant nature on the transformation mechanism was found. Ionogenic micelle-forming surfactants including a linear hydrocarbon fragment catalytically accelerate the decomposition of ROOH, whereas non-ionogenic surfactants soluble in RH and solid oxides practically do not affect the reaction rate. A detailed study of the kinetic regularities showed that the accelerating effect of surfactants is associated with their colloidal properties, namely, with the formation of joint aggregates such as inverted micelles, in which the decomposition of the peroxide bond is facilitated [2]. Synergism of the inhibitory action of sodium alkyl sulfate mixtures with phenolic antioxidants in the oxidation of various hydrocarbons has been established for the first time. At oxidation of ethylbenzene with small additives (<1%) of sodium dodecyl sulfate (SDS) a unique case of effective self-inhibition was established, the mechanism of which includes two positions: hydroperoxide - the main source of free radicals heterolytically decomposes in microaggregates jointly with SDS, the decomposition occurs selectively with formation of acetaldehyde and phenol; phenol, being an acceptor of free radicals, inhibits oxidation of ethylbenzene. Comparison of the results of kinetic studies, analysis of products during oxidation with surfactant additives revealed a number of chemical analogies in the action of surfactant microaggregates and acidic zeolite and superacid catalysts, namely: Olefin formation in the oxidation of dodecane and isopropylbenzene, structural specificity in the decomposition of ROOH, isomerisation and dehydrogenation of limonene in an inert atmosphere; similar effect of water on catalytic activity - promotion by microquantities and deactivation when the active surface is completely filled; and close dimensional characteristics. Rearrangements and cleavage of RH on zeolites, but in reversed micelles, which is very attractive, these reactions take place at much lower temperatures. Based on the results obtained, a hypothesis about the similar structure of the catalytic microreactor of RH and ROOH transformation in reversed micelles-microemulsions of ionogenic surfactants and in micropores of zeolites, the essential role of geometric and volume factor, curvature of the pseudo-surfactant interface in the catalytic transformation was put forward.

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THERMODYNAMIC APPROACH FOR THE DESCRIPTION OF NON-EXCHANGE SORPTION OF SUBSTANCES BY ION EXCHANGERS

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Ion exchangers, which are actively used for the separation, purification and concentration of electrolytes, equivalently exchange ions with the solution phase, but require further regeneration to restore the original ionic form. Thermodynamics, kinetics and dynamics devices have been developed for this process. Non-exchange absorption of substances by ion exchangers does not lead to a change in the ionic form of the sorbent, proceeds due to the action of specific forces and does not require subsequent regeneration of sorbents. Non-exchange sorption of substances by ion exchangers is possible if the absorbed particle is neutral, and the ion exchanger is used in any ionic form, if the substance is used in the form of a bipolar ion, and the ionic form of the ion exchanger is saline, which excludes recharging and subsequent ion exchange fixation of the substance, if the counterion of the ion exchanger, the absorbed substance and the medium-creating electrolyte coincide. A special case of non-exchange absorption is superequivalent sorption, a process of non-exchange absorption of substances that occurs together with ion exchange both in parallel and after its completion. The development of a unified thermodynamic approach to describe the non-exchange sorption of substances by ion exchangers is relevant.

The developed thermodynamic approach is based on the idea of stoichiometry of the process, when a certain number of particles of the absorbed substance account for one sorption center. The sorption center in ion exchangers, unlike nonionic sorbents, are functional groups with counterions. The stoichiometry coefficient in each system is found based on the quantitative characteristics of sorption, taking into account the nature of the absorbed substance and the method of fixation in the ion exchanger phase. The thermodynamic description provides for the choice of a comparison state (standard and/or reference), finding and interpreting the activity coefficients of the components of the solution and sorbent phases, finding thermodynamic equilibrium constants, integral and differential values of Gibbs energy, enthalpy and entropy of the process.

To find thermodynamic constants from the equilibrium coefficients obtained from experimental data (sorption isotherms) and taking into account the physico-chemical characteristics of the sorbate and sorbent, it is necessary to find the activity coefficients of the sorbent phase components. This is achieved by solving a system consisting of a logarithmic and differentiated equation of the corrected equilibrium coefficient and the Gibbs-Dugem equation for the sorbent phase. Next, the energy characteristics of the sorption process are found.

Knowledge of the equilibrium coefficients, the activity coefficients of the sorbent phase components, differential enthalpies and Gibbs energies related to an ion exchanger of a certain composition allows us to analyze the change in the state of the system at various stages of sorption. Thermodynamic equilibrium constants, integral quantities ΔG, ΔH, $T\Delta S$ characterize the overall transition of the system as a result of sorption from one state of comparison to another.In the case of the description of superequivalent sorption, two stoichiometric processes must be considered – ion exchange and non-exchange absorption. It should be borne in mind that the particle absorbed due to ion exchange is a sorption center for non-exchange absorption of the same substance (i.e., the basis of superequivalent absorption are sorbate-sorbate interactions).

In the case of considering multicomponent systems for both non-exchange sorption and superequivalent absorption, the system increases by the required number of equations.

THERMODYNAMIC DESCRIPTION OF NON-EXCHANGE SORPTION OF AROMATIC AMINO ACIDS BY ION EXCHANGERS OF VARIOUS TYPES

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Non–exchange sorption of substances by ion exchangers is one of the possible absorption mechanisms. At the same time, a distinctive feature from sorption on nonionic sorbents is the presence of fixed groups in the ionite phase. On the one hand, they prevent the absorption of the substance, and, on the other hand, they can be sorption centers. The nature of functional groups and counterions can be different, while the fixation of polar (ionized) particles of the absorbed substance is carried out due to in-ion and ion-dipole interactions with the counterion (in the absence of the possibility of recharging and ion exchange fixation).

The non-exchange sorption of aromatic amino acids tryptophan and phenylalanine from aqueous solutions with low- and high-base anion exchangers AN-251, AN-221, AB-17-2P in Cl form, weakly and strongly acidic cation exchangers KB-4P-2 and KU-2-8 in Na form, polyampholites ANKB-50 and ANKB-2 in salt form, etc. Since amino acids in aqueous solution have a positively charged amino group and a negatively charged carboxyl group, non-exchange sorption occurs on all types of ion exchangers used due to interaction with sorption centers of any nature.

A thermodynamic description of the sorption equilibrium in the systems under consideration is carried out based on the idea of stoichiometry of non-exchangeable absorption of substances, when a certain number of particles of the absorbed substance account for one sorption center. The stoichiometry coefficient is calculated as the ratio of the amount of absorbed substance to the number of sorption centers (total exchange capacity). To find thermodynamic constants from the equilibrium coefficients obtained from experimental data (sorption isotherms) and taking into account the physico-chemical characteristics of the sorbate and sorbent, it is necessary to find the activity coefficients of the sorbent phase components. This is achieved by solving a system consisting of a logarithmic and differentiated equation of the corrected equilibrium coefficient and the Gibbs-Dugem equation for the sorbent phase. Next, the energy characteristics of the sorption process are found.

For the thermodynamic description of the studied systems, the equilibrium of ion exchangers in the initial monoionic form with water was chosen as the state of comparison. Equilibrium coefficients, activity coefficients of sorbent phase components, thermodynamic equilibrium constants, integral and differential Gibbs energies of non-exchange sorption are calculated.

It was found that non-exchange sorption is greater on well-swelling sorbents with high capacity, while tryptophan is absorbed better than phenylalanine on all ion exchangers. The values of the equilibrium coefficients of non-exchange sorption of amino acids by ion exchangers obtained from sorption isotherms are mainly determined by the ratio of the number of sorption centers and the absorbed substance in the sorbent. The calculated coefficients of activity of free sorption centers deviate little from the state of comparison (from one), and the values of the coefficients of activity of sorption centers associated with sorbed amino acids are determined by the amount of absorbed substance. The obtained thermodynamic equilibrium constants of non-exchange sorption of amino acids are close to one. The Gibbs differential energies related to an ion exchanger of a certain composition increase during sorption, and the integral values are determined by the nature of the sorbed substance (the equilibrium constant).

PUZZLEZ OF PHASE REGIONS AND THEIR COMPLEX ELEMENTS FOR THE VIRTUAL $^{ep}Q>P_{ee}$ AND REAL Ag-Cu-Ni (A-B-C) DIAGRAMS

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Manual «Development of technical specifications for prototyping exploded T-x-y diagrams (Excel+AutoCAD technology)» of M.Parfenova, V.Lutsyk and M.Lamueva has been published by Banzarov Buryat State University in 2021. It was advertised at the India-Russia Scientific Webinar on Additive Manufacturing Technologies, 17 February 2022 (V. Lutsyk. Exploded phase diagrams (PD) of ternary systems: 3D-prototyping, correction, validation) https://indianembassy-moscow.gov.in/pdf/snt/India%20-%20Russia%20Scientific%20Webinar%20on%20Additive%20Manufacturing%20Technologies%20-%2017%20Feb%202022.pdf. Two variants of exploded PD have been used (A.Prince and M.Parfenova): to show all phase regions of PD or their compressed variant – a puzzle with complex element.

13 phase regions of N^{n1n2n3} eutectic-type diagram (N≡E,Q,P; n_i≡e,p) have been transformed into a puzzle of 4 typical 1(2 or 3 – but with liquid)-phase regions plus a 3-phase subsolidus region and complex element of the rest 8 regions, and 20 phase regions of diagram $^{n1n2}N1>N2(n_3n_4)$, where N1≡Q; N2≡E,Q,P; n_i≡e,p, with incongruent binary compound δ - to 10 phase regions and complex element (Fig. 1, to the left).

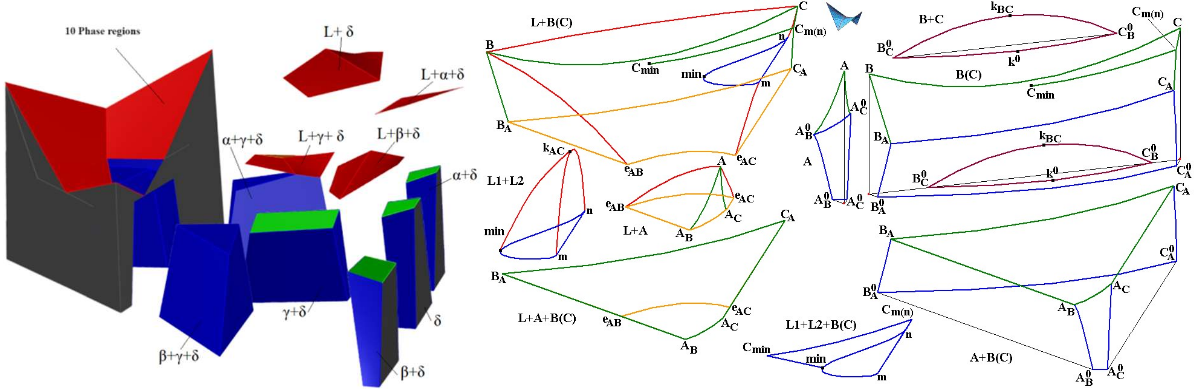

Figure 1. Puzzle of ten phase regions and complex element for diagram $^{ep}Q>P_{ee}$ (to the left); Phase regions of Ag–Cu–Ni (A–B–C) T–x–y diagram [1] (to the right)

Along with an expansion of the opportunities of computer design, it is pertinent that 3D models of PD (both for real systems and their prototypes) are helpful to recognize graphic errors in erroneous interpretation of experimental and computational (thermodynamic or ab initio) data. E.g., within T-x-y diagram with 3-phase equilibrium (terminology of A. Prince) comprising as few as six phase regions, two binary eutectic points are erroneously connected by two lines, rather than one (cited in [1]). The Ag–Cu–Ni diagram, comprising in addition three new phase regions, namely L1+L2, L1+L2+B(C), and B+C (Fig. 1, to the right), is derived from such a diagram. For this diagram it has been shown (likewise erroneously) the Ag+Cu+Ni three-phase subsolidus region (cited in [1]), while the phase reaction scheme forbids its existence.

[1] V.P. Vorob'eva, V.I. Lutsyk, M.D. Parfenova, *Russian J. Inorganic Chemistry*, 2023, 68, 69.

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PROTOTYPES OF T-x-y DIAGRAMS A,B,C||Hal (A,C -ALKALINE & B – LANTHANIDE ELEMENTS, Hal - F, Cl)

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It is not uncommon for the one(two)-phase solid regions of T-x-y diagram to have the solidus and solvus lines and surfaces degenerated into the edges and lateral faces of a trigonal prism, which greatly complicates the study and interpretation of the phase diagram (PD). In such cases, it is necessary to create a PD prototype – model with the artificially stretched degenerated regions to simplify the understanding of the PD structure (Figure 1).

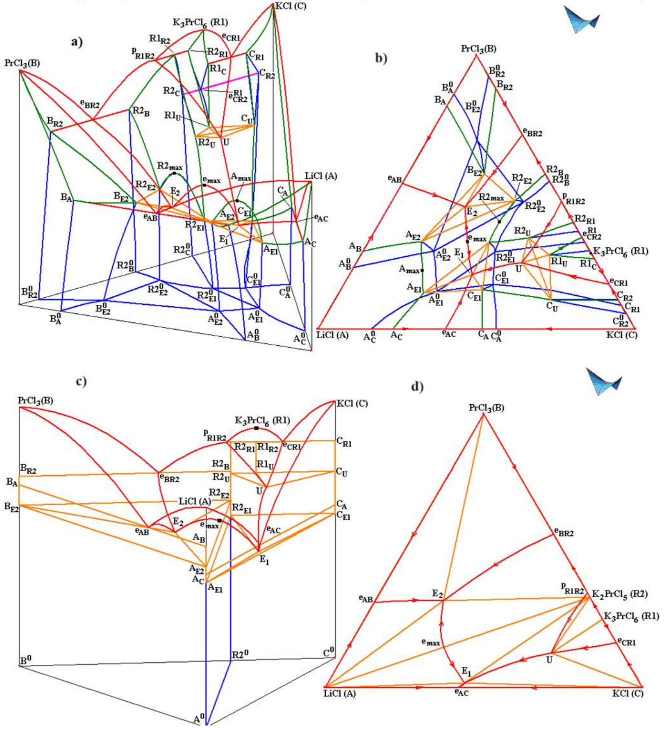

Figure 1. LiCl-PrCl$_3$-KCl phase diagram axonometric and concentration projections: (a-b) - prototype; (c-d) - real system [1]

In the study and practical use of multicomponent mixtures formed by halides, in the properties of which, as well as in the topologies of formed by them PD, there are many similarities, the following patterns can be distinguished: - at the first stage, their PD were studied experimentally, deciphering their DTA and X-ray phase analyses (XRD) spectra; then it was time to coordinate these results with the thermodynamic properties of the components, compounds and their liquid and solid solutions (this also includes PD calculations "from the first principles" or *ab initio*). Now the tasks of the materials science digitizing (assembling of PD spatial computer models, 3D printing of exploded phase regions and their puzzles, Materials Genome decoding by the phases trajectories simulation) have been appeared. 280 PD of A,B,C||Hal systems (for 5 alkaline and 14 lanthanide elements plus chlorine and fluorine) should be digitized by means of their prototypes with the identical topology (like PD for Li,Pr,K||Cl system [1], Figure 1).

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SELF-ORGANIZATION OF HYBRID LYOTROPIC LIQUID CRYSTAL AND CARBON DOT SYSTEMS IN MICROFLUIDIC CONFINEMENT

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Microfluidic devices with channel widths in the range of dozens and hundreds of micrometers offer new options for controlled self-organization of supramolecular systems and development of functional materials [1]. Among such media, liquid crystals attract particular interest for their ability to change molecular orientation and the resulting optical properties in response to wall effects, confined phase transitions, and shear [2]. Lyotropic liquid crystals [3] and their hybrids with optically active particles such as carbon dots allow to develop optofluidic devices with an optically active matrix for applications in photonics and biomedicine.

This work focuses on studying confined self-organization in a hybrid lyotropic liquid crystal and carbon dot system in microfluidic channels with 100-300 μm widths. Monododecyl ether of tetraethylene glycol in aqueous decanol media was used as a lyotropic liquid crystal.

Microfluidic confinement can provide controlled equilibrium or non-equilibrium conditions for self-organization by creating tunable temperature and concentration gradients or shears. In equilibrium static conditions (after injection into a microchannel), the liquid crystal system was shown to exhibit the lamellar mesophase, respectively. Self-organization of mesophase molecules near microchannel walls was found to be strongly influenced by phase transition inside a microchannel. After mesophase to isotropic phase transition and further cooling of microfluidic liquid crystal media, a predominant equilibrium orientation of molecules in the resulting static lamellar or hexagonal mesophases was found to be homeotropic (perpendicular to the interfacial boundary). Further shear of such textures with average flow velocities up to 1 mm/s created non-equilibrium stationary flow conditions with a predominant axial molecular orientation of mesophase molecules, which remained stable after stopping the flow.

After doping the studied liquid crystal systems with carbon dots (0.1 g/l), their orientation structures maintained both in static and dynamic conditions of microfluidic experiments. Such composites exhibited stable and uniform blue luminescence from carbon dots in all the studied flow velocity range.

The observed self-organization behavior of a lyotropic liquid crystal and carbon dot hybrid in static and dynamic microfluidic confinement contribute to development of microfluidic devices with integrated optically active functional materials sensitive to temperature and shear factors.

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TEMPERATURE, THERMODYNAMIC AND KINETIC CHARACTERISTICS OF THE PROCESSES OF FORMATION OF Eu_2MeO_6 (Me – Mo, W) AND $Eu_2W_2O_9$ COMPOUNDS

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The study of phase formation in binary oxide systems for the compositions $1Eu_2O_3$:$1MeO_3$ and $1Eu_2O_3$:$2MeO_3$ (Me – Mo, W) was carried out employing differential scanning calorimetry (DSC). In all cases, heat release corresponding to a one-stage interaction was recorded (Fig. 1). According to X-ray phase analysis of samples after DSC, the interaction leads to the production of single-phase samples Eu_2MeO_6 (Me – Mo, W) and $Eu_2W_2O_9$. The chemical interaction between simple oxides is described by the following reaction equations: $Eu_2O_3+MeO_3 = Eu_2MeO_6$ (Me – Mo, W) and $Eu_2O_3+2WO_3 = Eu_2W_2O_9$.

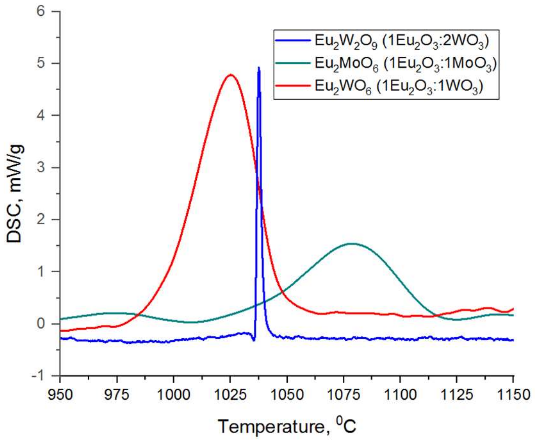

Figure 1. DSC curves of the interaction of simple oxides of the compositions $1Eu_2O_3$:$1MeO_3$ (Me – Mo, W) and $1Eu_2O_3$:$2WO_3$ at a heating rate of 5 degrees per minute.

To establish the temperature, thermodynamic and kinetic characteristics of the processes of formation of complex oxides, DSC was carried out at different heating rates of the samples. The obtained results are presented in Table 1.

Table 1. Temperature, thermodynamic and kinetic parameters of the formation of Eu_2MeO_6 (Me – Mo, W) and $Eu_2W_2O_9$ compounds.

Consist	Temperature range of reaction, °C	ΔH, kJ/mol	E_A, kJ/mol	A
$1Eu_2O_3$:$1MoO_3$	1010 – 1125	-37,0008	500	$4*10^{16}$
$1Eu_2O_3$:$1WO_3$	945 – 1065	-31,4962	233	$3*10^{6}$
$1Eu_2O_3$:$2WO_3$	1035 – 1045	-24,5458	6250	$6*10^{247}$

A characteristic feature of the systems studied is the formation of Eu_2MeO_6 compounds in a fairly wide temperature range. While the formation of the $Eu_2W_2O_9$ compound occurs very quickly in the range of only ≈10°C. Perhaps this indicates that the formation of $Eu_2W_2O_9$ at sufficiently high heating rates occurs through a more complex mechanism than was previously presented. It can be assumed that the process should occur in two stages: $Eu_2O_3+WO_3 = Eu_2WO_6$ and $Eu_2WO_6+WO_3=Eu_2W_2O_9$.

Carrying out the process at very low heating rates to differentiate the expected stages is technically difficult. The study of the $Eu_2WO_6+WO_3$ mixture by DSC seems promising. This will enable a more accurate assessment of the kinetic parameters, potentially revealing the detailed mechanism of the $Eu_2W_2O_9$ formation.

REDOX POTENTIALS IN NANOCLUSTER POLYOXOMETHALLATES IN SOLUTIONS AND IN SOLID STATE

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Nanocluster polyoxomethallates (POM), containing molybdenum, are of interest as materials that can be used in biomedicine [1] (targeted delivery of drugs), catalysis [2], sensory technology, template synthesis of polyfunctional systems [3].

The above unique objects have a number of physicochemical features both in the solid state and in solutions. Thus, photochemical degradation of POM Mo_{132} $\{(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(H_3CCOO)_{30}(H_2O)_{72}]\cdot(\sim300H_2O)\cdot(\sim10CH_3COONH_4)\}$ $\{(NH4)_{42}$ can be accompanied by fluctuations in absorbance [1, 3]. One of the versions explaining such fluctuations at the upper location of the irradiating diode is associated with reversible destruction of the POM. On the other hand, the measurements showed the presence of an increasing potential difference (Pt electrodes) up to 100 mV between the upper and lower parts of the POM aqueous solution in the measuring cell with fluctuations of this value (up to 20 mV) in time. The occurrence of the potential difference can be related to different ratios Mo (VI)/Mo (V) [4] above and below. Destruction of POM and oxidation of molybdenum with increasing acidity of the medium proceed more intensively in the upper irradiated part, which has contact with air or argon, which also, judging by the analyzes, contains some oxygen. The lower part of the solution is substantially shielded from light. Fluctuations in the potential difference, as well as in the optical density in the narrow beam of the spectrophotometer, can be associated with the observed periodic polarization and depolarization of the electrodes, since the diffusion coefficients of POM anions and excess hydroxonium cations differ significantly. Thus, the flux of POM ions in the beam of the spectrophotometer, which determines the optical density of the solution, at fluctuations in the potential difference, can also have fluctuations. The Gibbs energy calculation of a single electron redox reaction from the potential difference gives an order -2,2 kJ/mol, equilibrium constants 2.45, which indicates the possibility of a reversible course of said reaction.

Thermal decomposition processes of Mo_{132} are accompanied by generation of charges in the heated solid sample. In this case, depending on the presence of an external electromagnetic field or in its absence, the ground-precursor potential difference can vary from 120 V to -120 V, which is associated with the release of amphiphilic substances: acetamide, acetonitrile [5] into the enveloping environment during destruction of POM. Molecules of such compounds can ionize negatively under the influence of a field that promotes the emission of electrons by a precursor, or positively, giving up electrons to the sample.

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LOW-TEMPERATURE HEAT CAPACITY OF SOME HORMONES

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Hormones are one of the most important biologically active substances. They are vital and necessary compounds, each of which plays an indispensable and very important role in the vital activity of the organism. Hormones are the products of internal secretion, which are produced by special glands or individual cells, are secreted into the blood and spread throughout the body, causing a certain biological effect. These substances have always been of interest to chemistry in terms of their synthesis. However, not only the preparation of the compound is important, but also information on its physicochemical properties and structural characteristics. The investigation allowed a comprehensive study of the physicochemical properties and structure of steroid hormones, such as methylprednisolone aceponate, methylprednisolone, betamethasone valerate and mometasone furoate [1-3]. The calorimetric determination of the temperature dependences of the heat capacity of these compounds in the range from 6 to 350 K is carried out and standard thermodynamic functions are calculated: heat capacity, enthalpy, entropy and the Gibbs function of heating in the temperature range of 0 - 350K. The type of topology structure is determined according to the data of multifractal processing of low-temperature heat capacity. The heat capacity of all substances, except methylprednisolone aceponate (MPA), gradually increases with rising temperature and does not show any peculiarities. We discovered anomalous behavior of the heat capacity for MPA in the temperature range 102 to 140 K. The transition temperature of the sample under study 131.0 ± 0.1 K was estimated as the temperature of maximal heat capacity value within the temperature interval of the transition and the standard uncertainty of phase-transition temperature is 0.1 K. The standard enthalpy of phase transition is $\Delta_{tr}H° = 220 \pm 2$ J·mol^{-1}. The ordering of the MPA molecules along the crystallographic direction [010] is observed after the phase transition at T = 131K, which leads to an additional translation o **b**/3. As a result, the orientation of the methyl groups becomes chaotic and the translational symmetry disappears for these groups. The atomic structure at 90K have a translational pseudosymmetry of electron density η=0.329(1). In addition, we have applied the method of molecular Voronoi−Dirichlet polyhedra (MMVDP) for analysis of differences in intermolecular contacts in MPA crystals. According to the obtained data, 4 (for modification I) and 5 (for modification II) of the 6 theoretically possible (as the compound comprises atoms of three elements) types of A/Z intermolecular contacts are actually implemented in structures. Thus, we observe the decrease of number of intermolecular contacts in the high-temperature modification due to rupture of intermolecular non-valence contacts C/O. We are currently conducting research on heteroauxin, which is a phytohormone (plant growth hormone).

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STUDY OF THE TRIPLE SYSTEM Pr-Bi-Te

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Chalcogenides of rare earth elements and elements of the arsenic subgroup, in particular antimony and bismuth, have valuable optical and electrophysical properties for use in thermoelectric and optical devices [1-3]. Bismuth chalcogenides of the composition Bi_2X_3(X-Se,Te) and solid solutions based on them are used as thermoelectric material in the manufacture of p and p branches of thermoelectric devices. Therefore, the study of the Pr-Bi-Te ternary system is relevant. Alloys of the Pr-Bi-Te system were synthesized by the ampoule method in a single-temperature vertical furnace at 900-1450K. The initial samples of the system were synthesized from elements of high purity: Bi-grade B-4, Pr-metallic Prt-0, Te grade Te-A2. The synthesis mode was selected based on the physicochemical properties of the starting materials.

Alloys with a content below 60 mol% are compact, dark gray in color with a metallic sheen. To obtain an equilibrium state, the alloys were subjected to homogenizing annealing in evacuated quartz ampoules at a temperature of 50-70 K below Solidus for 750 hours. The study was carried out using differential thermal (DTA), high-temperature differential thermal (HDTA), X-ray diffraction (XRF), and microstructural (MSA) methods.) analyzes and microhardness measurements. When studying the microstructure of alloys, an etchant with the composition $0.1 \cdot K_2Cr_2O_7 \cdot H_2SO_4 + H_2O$ (1:1) was used. Taking into account the analysis results, it has been established that the cuts of the Pr-Bi-Te system are quasi-binary and belong to the eutectic type. The nature of the interaction in quasi-binary cuts of the Pr-Bi-Te system is given in Table 1.

Table 1. The nature of interaction in quasi-binary cuts of the Pr-Bi-Te system.

Cuts	Eutectic coordinates	Composition of Pr based on Bi_2Te_3, mol %
Bi_2Te_3-PrTe	80 Bi_2Te_3, 800K	3 PrTe
Bi_2Te_3-Pr_3Te_4	80 Bi_2Te_3, 600K	5 Pr_3Te_4
Bi_2Te_3-Pr_2Te_3*	70 Bi_2Te_3, 800K	5 Pr_2Te_3
PrTe- Bi	94 Bi, 515K	-
PrTe- PrBi	45 rBi, 1300K	-

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THE SOLUBILITY AND THERMODYNAMIC PROPERTIES OF SYNTHETIC HYDROXYSALTS OF TRANSITION METALS

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Thermodynamic parameters of oxidized minerals of transition metals (copper, zinc, nickel, etc.) are important when studying minerals in the oxidation zone of deposits, corrosion of alloys, immobilization of heavy metals, obtaining new materials, etc. However, for a number of the compounds, the measured values of the solubility product and thermodynamic functions are different or absent at all. The solubility of the synthetic nickel hydroxycarbonate and copper hydroxosulfates were studied and thermodynamic properties were obtained.

The synthesis procedure was carried out by hydrothermal synthesis in autoclave fluoroplastic vessel at 90°C. The obtained samples were characterized by Fourier transform infrared spectroscopy and X-ray diffraction analysis with a good degree of reliability.

To study the thermodynamic characteristics of the synthesized samples, experiments on their dissolution were carried out at temperatures of 20, 50 and 80°C for several weeks. The concentration of transitional metal ions in the solutions was determined every few days by spectrophotometric analysis. The asymptotic values of the function were taken as the equilibrium concentrations of ions in solution to determine the dissolution constants.

The parameters for temperature dependences of the dissolution constants were found and thermodynamic functions of the dissolution reaction are calculated on their basis.

The values of the Gibbs free energy of formation $\Delta_f G^\circ$, the enthalpy of formation $\Delta_f H^\circ$ and the standard entropy S° of the compound were calculated in accordance with Hess's law. The values of the thermodynamic functions of individual ions required for calculation were taken from the base reference book on the thermodynamic properties of minerals [1].

Standard thermodynamic functions of synthetic hydroxysalts are shown in the table.

Value	$Ni_3[CO_3](OH)_4\cdot 3H_2O$	$Cu_3[SO_4](OH)_4$	$Cu_4[SO_4](OH)_6$	Units
$\Delta_f G^\circ$	−1554±6	−1460.6±6.2	−1819.8±10.9	kJ/mol
$\Delta_f H^\circ$	−1798±9	−1743.3±43.6	−2179.7±23.2	kJ/mol
S°	260.6±7.8	266.8±40.0	377.4±169.2	J/(mol·K)

The obtained values of the thermodynamic functions are in satisfactory agreement with the both calculated and experimental data for natural minerals and similar compounds.

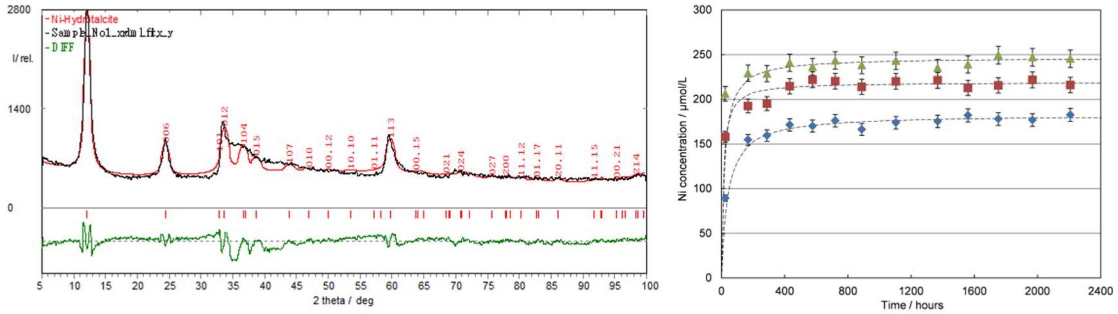

Figure. X-ray pattern and ion concentration at various temperatures for $Ni_3[CO_3](OH)_4$

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