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BOOK OF ABSTRACTS

29th International Conference on Solution Chemistry

August 21st – 25th, 2005
Portorož, Slovenia

Dear colleagues and friends,

Welcome to the 29th International Conference on Solution Chemistry and to Slovenia. We can now add Portorož to the list of past conference sites such as Debrecen, Vaals, Fukuoka, and other cities in the long tradition of Solution Chemistry Conferences.

29th ICSC is, as many previous conferences, sponsored by the International Union of Pure and Applied Chemistry, being this way recognized for its excellence. The conference theme is the chemistry of solutions but it also includes areas such as Supramolecular assemblies and nanostructures, Interfaces, Aquatic Chemistry, and others. Another interesting addition to the program is a round table discussion on Ionic Liquids. The list of invited lecturers speaks for itself and indicates a broad distribution of topics and outstanding quality of participants.

29th ICSC is truly a world conference with participants from 36 countries. Furthermore, we are particularly proud that we have 50 student participants. We are equally happy to greet over 30 accompanying persons which make the conference a family event. We have prepared a rich social program for them as also for the other participants.

The organizers made strong efforts to secure funds for participants from economically less developed countries. More than 30 participants are fully sponsored by the Organizing Committee. This could never be possible without generous donations from Organization for Prohibition of Chemical Weapons, The International Union of Pure and Applied Chemistry, and Slovenian Research Agency. We also owe gratitude to many other donators and sponsors which are listed later in this Book. We are particularly thankful to our general sponsor Lek, a new Sandoz company, from Ljubljana.

We hope sincerely that the St. Bernardin Convention Centre and favourable Mediterranean climate of Portorož will contribute to a pleasant and stimulating working atmosphere. On behalf of the Organising Committee, I thank you for your contribution to the success of this Conference.

We wish you a pleasant stay in Slovenia!

Sincerely,

Professor Vojko Vlachy,
Chairman of the Organizing Committee

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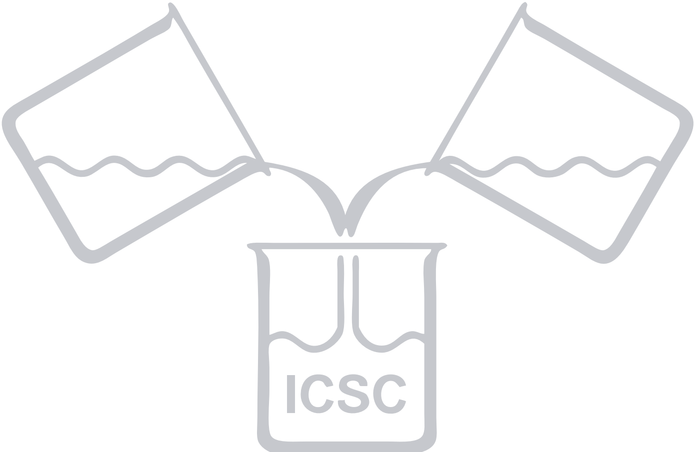

From Supramolecular Chemistry to Constitutional Dynamic Chemistry

Jean-Marie Lehn
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Supramolecular chemistry is intrinsically a dynamic chemistry in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their constituents. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a Constitutional Dynamic Chemistry (CDC) on both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. The latter relies on design for the generation of a target entity, whereas CDC takes advantage of dynamic diversity to allow variation and selection. The implementation of selection in chemistry introduces a fundamental change in outlook. It operates on dynamic constitutional diversity in response to either internal or external factors to achieve adaptation.

Several applications of this approach in biological systems as well as in materials science will be described.

The merging of the features: - information and programmability, - dynamics and reversibility, - constitution and structural diversity, points towards the emergence of adaptive chemistry.

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Modeling Water, the Hydrophobic Effect, and Ion Solvation

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We have developed simple statistical mechanical models of water, for understanding water's physical properties in the pure liquid and for understanding water as a solvent for hydrophobic solutes and ions. We start with the Mercedes-Benz model, in which water is simplified to be 2-dimensional disks with 3 radial hydrogen bonding arms, configured as in the Mercedes-Benz logo. We study the model by Monte Carlo simulations, and we now also have analytical versions of it. We find that these models, despite their simplicity, can capture many features of real water, and give insights into the underlying physical bases for those properties.[1]

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Small-Angle X-Ray Scattering of Hierarchically Organized Lipid Systems

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and Heribert Watzke[2]
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Aqueous sub-micron sized dispersions of the binary monolinolein/water system, which are stabilized by means of a polymer, internally possess a nano-structure. Taking this as our starting point, we were able to demonstrate for the first time that this internal structure can be tuned by temperature in a reversible way. Upon increasing the temperature, this internal structure undergoes a transition from cubic via hexagonal to a fluid isotropic, so-called L_2-phase and vice versa. This means that upon cooling there is also a back transformation of the internal structure from L_2 via hexagonal to cubic. We found that these internal structures depend only on the current temperature and there is no hysteresis or other change after such a heating/cooling cycle. Intriguingly, in addition to the structural changes in topology, the particles exhibit a "breathing mode": they expel (take up) water to (from) the aqueous continuous phase when increasing (decreasing) the temperature in a reversible way. At each temperature, the internal structures of the dispersed particles correspond very well to those in non-dispersed binary monolinolein-water phase with excess water. This proves that they actually remain in thermodynamic equilibrium even though the particles themselves are kinetically stabilized.[1] They are internally self-assembled ("ISASOMES").
Recently we were able to incorporate also additional oil into the system and thereby controlling the resulting structures at a given temperature. This finally led, for the first time, to the formation of emulisified micro-emulsions.[2] We also discovered of an Fd3m phase (reversed discontinuous micellar cubic), which is formed in the MLO-water-tetradecane (TC) system at a specific TC/MLO weight ratio. It is situated between the H_2 and the isotropic liquid phase (w/o microemulsion). Remarkably, it is not found in the absence of TC by increasing the temperature.

All structures were investigated in detail by means of Small Angle X-ray scattering (SAXS), and cryogenic transmission electron microscopy (Cryo-TEM). All the different ISASOMES have internally a huge interfacial area which can be used for many different types of applications.

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Are Ionic Liquids Liquid or Just Runny Solids?

D. T. Bowron[1], M. Deetlefs[2], C. Hardacre[3], J. D. Holbrey[3], S. E. J. McMath[2],
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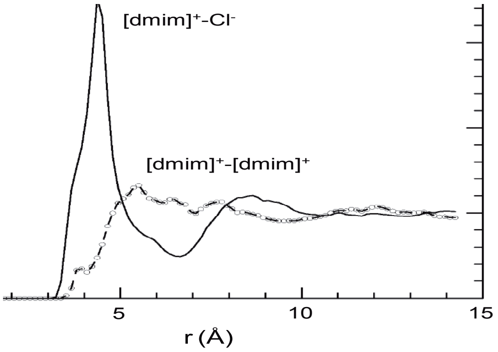

Figure 1 Partial radial distribution functions for the cation-cation distribution (circles+line) and the cation-anion distribution (line) derived from the EPSR model. Each radial distribution function is calculated from centre of theimidazolium ring.

Room temperature ionic liquids represent a new class of solvents in which to perform chemical reactions. Ionic liquids comprising exclusively of ions, which have a unique set of properties including effectively zero vapour pressure. These properties have led to the extension of ionic liquids as environmentally benign solvents for applications in "green chemistry". Many of their properties are determined by the structure within the liquid and although considerable research has been performed on the structure of molten salts, little is known about the liquid structure of ionic liquids. This is crucial if an understanding is to be obtained with regard to their solvent and reactive properties, which have been studied extensively. Neutron and X-ray diffraction techniques have been used to study the interactions between the ions in the liquid state.

The liquid structure of 1,3-dimethyl imidazolium ([dmim]$^+$) chloride, hexafluorophosphate and bis(trifluorosulfonyl)imide salts has been determined using neutron diffraction. In order to analyse and interpret the data obtained an empirical potential structure refinement process (EPSR) was used. From the data it is clear that in each case strong cation-anion ordering is found in the liquid state as indicated by the partial radial distribution function for the cation-anion and cation-cation interactions in Figure 1 for [dmim]Cl. Similar distributions are observed for each of the ionic liquid systems studied. Figure 2 compares the anion-cation probability distributions of the hexafluorophosphate anion and the chloride anion around a central imidazolium cation in [dmim][PF$_6$] and [dmim]Cl. It is clear that significant differences are observed in the first anion shell. The strong interaction of the chloride with the hydrogen attached to the C(2) carbon indicates that hydrogen bonding dominates the structure. In comparison, the hexafluorophosphate anion is a much weaker hydrogen bonding species and prefers to interact with the ring. If the cation-cation distributions are compared for each of these salts, the differences become even more apparent whereby the size of the hexafluorophosphate compared with the chloride prevents close contact between the cations and the cations and anions form mutually exclusive distributions.This presentation will focus on the liquid structure and relate the structures found with single crystal X-ray diffraction data on these salts. The results will also be correlated with findings from molecular dynamic simulations. The structures of both long and short chain length ionic liquids will be presented.

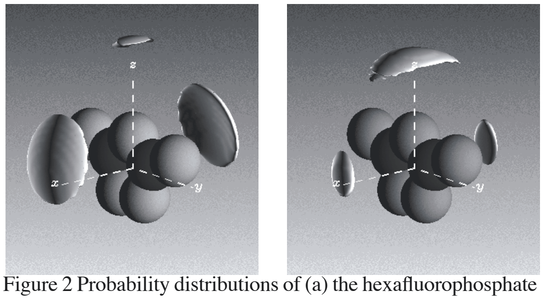

Figure 2 Probability distributions of (a) the hexafluorophosphate anion and (b) the chloride anion around a central imidazolium cation in [dmim][PF$_6$] and [dmim]Cl, respectively, derived from the EPSR model. In each case the distributions are the probability of finding 2.5 % of the ions out to a distance of 9 Å.

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When Spectroscopy Fails: the Measurement of Ion Pairing

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There is no doubt that techniques such as UV-Visible, NMR and Raman spectroscopies are extremely powerful tools for the investigation of chemical speciation (complex formation, ion association) in solution. However, it is not widely recognized that such techniques do not always provide reliable information about equilibria in solution. Specifically, spectroscopic measurements do not in general produce thermodynamically meaningful association constants for non-contact ion pairs, i.e., species where the ions are separated by one or more solvent molecules. Such systems can only be properly quantified by techniques such as dielectric or ultrasonic relaxation, which are (at least in principle) able to detect all ion-pair types, or by traditional thermodynamic methods, which detect the overall level of association.

The failure of spectroscopic methods under these circumstances occurs because the perturbation of the spectroscopically-active moiety by the complexing/associating species, which constitutes the information regarding complexation/association, is generally too small to be detected as a result of attenuation by the intervening solvent molecules in non-contact species.

These effects will be illustrated mostly using quantitative data for apparently ‘simple’ metal ion/sulfate systems. Various types of spectroscopic and other data will be presented that demonstrate the inadequacy of the major spectroscopic techniques for the investigation of systems that involve non-contact ion pairs.

Specific Ion Effects in Colloids, in Biological Systems and at Interfaces[1]

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Ions are, of course, much more than charged hard spheres. Nevertheless, their specificity is often not explicitly taken into account in complex systems, such as colloidal phases or biological environments. If it is really done, their individual influence on the system is characterized with expressions like “soft” or “hard” ions, “cosmotropic” and “chaotropic” behaviour, or, often taken as synonyms: “polarizable” or “hydrophobic” and “unpolarizable” or “hydrophilic” ions.

In the present talk, I want to give a survey on some striking experimental evidences of the so-called “Hofmeister series” of ion specificity. Recent theoretical and simulation approaches to the quantitative description (and prediction) of specific ion effects will also be discussed. And finally, a fascinating example of self-organization in ionic solutions leading to new and highly ordered materials will also be presented.

[1] Those who are interested in specific ion effects can find a compilation of recent research efforts in the special volume:
Current Opinion of Colloid and Interface Science (W. Kunz, P. LoNostro, B.W. Ninham (Guest Editors)) Vol. 9 (1-2) (2004).

Shipwrecks, Sulphur, Acid and Iron; the Vasa‘s New Battle

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The anoxic conditions predominating at the seabed and in bottom sediments sometimes enable high levels of preservation of wooden marine-archaeological artefacts, as for the Swedish warship *Vasa* from 1628 (Figure 1). However, stable conservation of degraded waterlogged wood infested with sulfur and iron compounds, is a difficult task. Synchrotron-based sulfur K-edge x-ray absorption near edge structure (XANES) spectroscopy (SSRL, beamline 6-2) has made sulfur speciation possible for natural samples, and revealed when applied on the *Vasa* that totally several tonnes of reduced sulfur compounds had unexpectedly accumulated in the hull timbers, with oxidation processes presently giving rise to severe acidity, see http://www.fos.se/~magnuss/.[1] Further XANES analyses of several historical shipwrecks, including the 16th century flagship of Henry VIII, the *Mary Rose,* Portsmouth, UK, show that sulfur and iron compounds often have accumulated in large quantities in the wood, with the penetration aided by wood-degrading bacterial activity. Recent x-ray spectro-microscopy studies (ESRF, beamline ID21) reveal that bacterially produced hydrogen sulfide, dissolved in the penetrating water, has reacted to form organosulfur compounds in lignin-rich parts of the marine-archaeological wood, together with iron sulfides in particles. Oxidation of the iron sulfides in the humid wood impregnated with polyethylene glycol, probably is the main cause of acidity, while the organosulfur compounds may be more resistant to oxidation. For lasting conservation, acid-forming sulfur compounds in the wood should be removed, together with extraction of iron ions with an efficient soluble chelate.[2,3] EDMA, ethylenediiminobis(2-hydroxy-4-methyl phenyl) acetic acid, derived from EDTA, is such an chelating agent and encloses iron(III) with six surrounding atoms in a well-fitting octahedral cage.[4] It can keep iron(III) ions dissolved in alkaline solution up to pH = 12, before goethite, FeOOH(s), precipitates, and is being tested for iron removal.

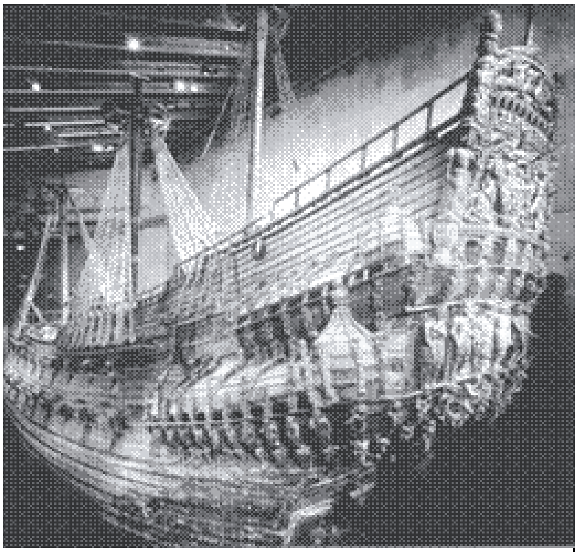

Figure 1: The *Vasa* after conservation treatment

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Multiscale Dynamics in Complex Ionic Media

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The characteristic feature of transport processes is their variation according to the time and distance of observation of the corresponding phenomenon. This variation is particularly spectacular in complex media, such as colloidal suspension and porous systems.

The understanding of the processes goes then, through specific experimental information at each stage of observation of the processes. Corresponding modelling is developed in order to infer specific parameters. The last stage is to reconstruct a general picture of the system, consistent with every level of description.

Examples are given on the dynamics of ions and water in clays, by neutron scattering, dielectric spectroscopy, molecular dynamics and several mesoscopic models.

Calorimetry as a Tool for Studying Molecular Recognition and Stability in Bio-Systems

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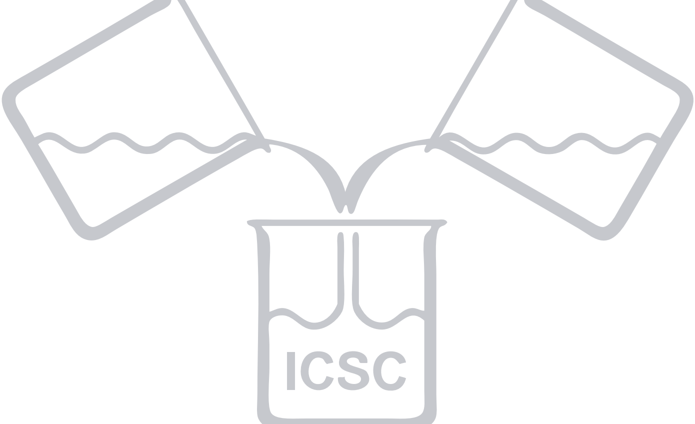
In recent years NMR and X-ray crystallography studies have provided a three-dimensional picture of nucleic acids and proteins and thus enabled us to recognize the structure-function relationship that characterizes the behavior of these macromolecules. Unfortunately, examination of structural features alone provides no information about the forces that drive the binding reactions or are responsible for the stability of the folded conformations of biological macromolecules in solution. Therefore, in order to gain a better understanding of these processes it is necessary to combine the known structure of species involved with the corresponding thermodynamics. Calorimetry is the only technique that directly and without the need of a predetermined model measures the energetics of the studied process. Order-disorder transitions such as protein unfolding or melting of nucleic acids can be studied using differential scanning calorimetry (DSC). By measuring the temperature dependence of the partial heat capacity of the solute, DSC leads straightforwardly to thermodynamics that characterizes the conformational equilibrium, for example between the folded and unfolded state of a protein, or between the double stranded DNA and its single strands. Ligand-macromolecule or macromolecule-macromolecule binding can be examined using isothermal titration calorimetry (ITC). Using this powerful technique for examining biochemical reactions one can determine the binding enthalpy, the binding constant and the reaction stoichiometry in a single experiment. By performing these experiments over a range of temperatures one can determine also the change in heat capacity. Since the absorption or evolution of heat is a universal property of chemical reactions ITC can be used to study almost any bimolecular complex formation. To demonstrate the versatility and power of DSC and ITC for elucidating thermodynamic information on macromolecular stability and molecular recognition examples from the literature as well as work conducted in our laboratory will be presented. In the last decade, numerous studies on protein stability and ligand binding to DNA have shown that the resulting changes in heat capacity, and in case of protein unfolding also the enthalpies of unfolding, can be related to changes in solvent accessible surface area accompanying these processes. A possibility of a successful correlation of structural features with the bulk thermodynamic parameters for processes involving ligand binding and conformational transitions of macromolecules in solution will be discussed.

KEYNOTE LECTURES



Entropy of Mixing and Entropy of Assimilation; an Information Theoretical View

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This lecture is addressed to anyone who has learned about „entropy of mixing"; Chemists, Biochemists and Physicists. It is more of an „educational", or of pedagogical character, than a research topic. Yet, some new ideas are presented that are not known to the majority of scientists. The main idea is that, contrary to what is written in most textbooks, mixing of ideal gases, in itself does not change any thermodynamic property of the system. Hence, thermodynamically speaking, it is a „non-process". The term „Entropy of Mixing" ascribed to the quantity $-k_B T \Sigma x_i \ln x_i$ is inappropriate, and the idea that „mixing" is an inherently irreversible process, is wrong. Instead the concepts of assimilation and de-assimilation are introduced, and it is shown that the process of de-assimilation is inherently irreversible (both for classical and quantum mechanical particles). The informational-theoretical aspects of mixing and assimilation processes, is also discussed. It is shown that while „Mixing", in itself does not change the information of the system, „Assimilation" does increase the information of the system.

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Hydration of Tetraphenylphosphonium and Tetraphenylborate Ions

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The splitting of the thermodynamic properties of electrolyte solutions into their ionic contributions requires an extra-thermodynamic assumption, such as the widely accepted tetraphenylarsonium tetraphenylborate (TATB) or tetraphenylphosphonium tetraphenylborate (TPTB) assumptions. The notion underlying the TATB/TPTB assumptions is that the anions and cations of either salt show similar and weak interactions with the solvent due to their large and similar radii, and the similarity of their exposed phenyl groups. In this way it becomes reasonable to assume, eg. for TPTB, that $X(TP^+) \approx X(TB^-) \approx \frac{1}{2} X(TPTB)$, where X is any appropriate thermodynamic quantity.

Whilst this approach has been widely employed, very few studies have been made on the nature of the ion-solvent interactions that underpin it. This is especially true for aqueous solutions where the insertion of large hydrophobic ions might be expected to have a significant influence on the structural and dynamical properties of the surrounding water molecules.

In this contribution we report results of a dielectric relaxation study of Ph_4PCl(aq), Ph_4PBr(aq) and $NaBPh_4$(aq). Dielectric relaxation spectra were measured over a wide range of frequencies ($0.2 \leq \nu/\mathrm{GHz} \leq 89$) at 25°C and analysed in terms of a number of superimposed dispersion steps. Specific to these electrolytes is the emergence of a relaxation process at ~9 GHz which can be attributed to water molecules adjacent to the hydrophobic Ph_4P^+ and BPh_4^- ions, whose dynamics are slowed down compared to those of bulk water. The hydration numbers of Ph_4P^+ and BPh_4^- decrease significantly with increasing electrolyte concentration. Simultaneously, a weak solute relaxation process appears. Both observations suggest some sort of ion clustering at $c > 0.1$ M to minimise the size of the hydrophobic surface exposed to water.

Reactive Intermediates in Aquoeous Ozone Decomposition. A Mechanistic Approach.

István Fábián

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In the last few decades, ozone has gained disputable fame because its disappearance from the stratosphere (ozone hole) and the detrimental effects it causes in the quality of air in urban areas. However, ozone is also an important industrial oxidant which finds widespread applications in advanced oxidation processes (AOP). Among others, hydrogen peroxide is the most frequently used agent to boost the reactivity of the oxidant in these systems. The role of promoters and inhibitors can be understood in terms of how they affect the production of reactive radicals, most prominently OH, during ozone decomposition. Thus, fairly detailed and accurate kinetic models of ozone decomposition are required in order to explore the chemical background of AOP-s and to maintain the optimum ozone budget in practical applications. The same models are also useful in the assessment of the environmental impacts of ozone.

Recently we have thoroughly studied the decomposition of ozone in the alkaline pH range (pH = 10.0 to 13.5) and developed a detailed kinetic model for the reaction using a comprehensive data treatment method.[1,2] The model gave appropriate interpretation of the experimental data under a variety of experimental conditions and could be used as a basis in further model development for the interpretation of carbonate ion inhibition[3] and hydrogen peroxide catalysis. The lecture will summarize new results in these studies and provide insight into the intimate details of a rather complex radical type chain mechanism.

First of all, it will be demonstrated that major controversies in previous literature are mainly due to inappropriate experimental protocols and the use of oversimplified models for the evaluation of the kinetic data. Our results confirm that H_2O_2 may accumulate at sufficiently high concentration levels during the preparation of acidic ozone stock solutions and significantly alter the life-time of ozone in subsequent kinetic experiments.

In our studies, the experimental data were collected using a wide range of carbonate ion and hydrogen peroxide concentrations both separately and in combination. Control experiments in the absence of catalyst and inhibitor were always run. The results were evaluated by fitting simultaneously up to 60 kinetic traces (ca 25,000 time dependent data points) recorded under various conditions at 260, 400 and 430 nm where ozone, carbonate ion radical and the ozonide ion radical have maximum absorbance, respectively. It will be shown that the use of such a comprehensive evaluation technique yields an improved set of rate constants for the individual reaction steps in the kinetic model and makes possible to eliminate the uncertainties related to the initial sequence of the overall process. The validity of the model under neutral and acidic conditions was also tested. It was found that apart from the initiation reaction the same chain carrier steps are operative in the entire pH range.

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Introductory Remarks on Thermodynamics of Ionic Liquid Solutions and Their Importance in Applied Science

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Ionic Liquids (ILs) are organic salts consisting of large asymmetric cations (e.g. imidazolium, pyridinium cations) and anions such as PF^-_6, BF^-_4, NTf_2 (bis(trifluoromethyl sulfonyl)imide) and others which exist in the liquid state at room temperature and below.

During the last years the interest in ionic liquids has increased dramatically for several reasons.

- The most striking property of ILs is their non detectable vapour pressure. This suggests the utilization of ILs as ideal solvents replacing conventional solvents in frame of a "green chemistry".
- Due to their highly polar character caused by coulomb forces acting between the ions in the liquid state ILs open new ways for chemical reactions in homogeneous as well as biphasic catalysis including biocatalysis.
- Some of the ILs show selective solubilities for particular components in fluid mixtures. These ILs are most interesting candidates for separation processes where they could serve as extraction media.
- Other fields of possible applications are the utilisation of ILs as lubricants, thermofluids, plastizisers and electrically conductive liquids in electrochemistry.

While the majority of research work has been focussed on organic synthesis of ILs and on the study of chemical reactions in ILs systematic investigations of thermodynamic and thermophysical properties of ILs and in particular of mixtures containing ILs are still rare. On the other side data of these properties are of considerable importance for selecting appropriate ILs and their mixtures in different applications of chemical engineering as mentioned above.

In this introductory contribution thermodynamic properties and transport properties of ILs and their mixtures with other liquids and compressed gases will be described and their importance for some selected fields of applications will be discussed.

Solvent Conformation and Ion Solvation –from Molecular to Ionic Liquid

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Metal-ion solvation is essential in the metal-ion complexation in solution. Structural studies have revealed that solvation number of a metal ion depends on the solvent, and that preferential solvation of a metal ion in solvent mixtures is not determined solely in terms of ion-solvent interactions. Solvation steric interaction, or solvent-solvent and/or ligand-solvent interaction through space in the coordination sphere of a metal ion plays also an important role. Solvation steric interaction operates particularly for organic solvents with a bulky functional group in the vicinity of the coordinating atom. It has been known that molecular geometry of solvent remains usually unchanged upon solvation, while the coordination geometry around the metal ion is distorted (weak solvation steric effect), or the solvation number is even reduced (strong solvation steric effect).

On the other hand, there found some solvents that change their molecular geometry upon solvation, and two conformers are present in equilibrium in the coordination sphere of the metal ion. Here, Raman spectrometry and theoretical DFT calculations are very useful tools for studying solvent conformation in the bulk and in the coordination sphere of the metal ion.

We will discuss conformation of N,N-dimethylpropionamide (DMPA), dimethylcarbonate (DMC), etc., as molecular liquids and of 1-ethyl 3-methyl imidazolium (EMI) bis-(trifluoromethanesulfonyl) imide (TFSI) and related compounds as ionic liquids. Calculated energy profiles of these solvents show possibility of presence of some conformers in the bulk and the enthalpy of conformational change was evaluated. The enthalpy change was indeed evaluated by Raman spectroscopy measured by varying temperature. We will also discuss individual solvation number of each conformer bound to the metal ion, and thermodynamic parameters of conformational change studied by Raman spectroscopy.[1] We will demonstrate that conformational equilibrium and related enthalpy and entropy values change sensitively depending on the ionic size and electronic configuration of the central metal ion.[2] These thermodynamic parameters also depend on the coordination number and geometry of the metal complex. Conformational geometry change and energy profile for solvent molecules bound to the metal ion were also studied by DFT calculations.

We will finally discuss the solvation steric effect on metal-ion complex formation reaction studied by calorimetry and spectrophotometry. It will be demonstrated that thermodynamic parameters, particularly enthalpy and entropy changes, of metal-ion complexation involve a large contribution of solvent conformational change.

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Electrolyte Distribution Around Two Like Charged Rods and Their Effective Attractive Interaction: Angular Induced Charge Polarization and Overcharging Effects

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We explored several conditions under which two charged rods, immersed in a primitive model electrolyte, experiment attraction. We found that attraction may occur even if the salt ions are monovalent, provided they have high volume fraction. For small monovalent or divalent ions at small to medium concentration no attraction is observed. For divalent electrolytes, attraction occurs only if salt concentration is sufficiently high. These findings point out the relevance of considering properly the entropic contribution to the effective rod-rod interaction[1-4]. The rod-rod effective interaction is discussed in terms of the electrolyte structure around them: there is a direct correlation between an angular induced charge polarization (and charge reversal) to their attraction. To the best of our knowledge this angular dependence of the potential and induced charge, as a function of the rods separation, have not been reported before. Our results are adquired by means of integral equation and mean field Poisson-Boltzmann theories calculations, and compared with our Monte Carlo[5] simulations. Integral equations and computer simulations are in good agreement, whereas Poisson-Boltzmann theory does not.

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Interfacial Studies of Alkyl-Phosphonate SAMs on Mica

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Layer formation of self-assembling molecules of alkyl-phosphonic acids has been followed by atomic force microscopy and dynamic contact angle measurements. The aggregation behavior of molecules in the solution phase and critical micelle concentration has been determined with surface tension measurements.

Nucleation, growth and coalescence of densely packed two-dimensional islands of phosphonates have been recorded on mica surface. In Figure 1a, the AFM image of 1-phosphono-octane layer can be seen on mica during the growth step, after 18 h of immersion. The height of islands is 1.4 nm, which is equal with the length of molecule. Figure 1b shows the structure of self-assembled layer of phosphono-octane after 60 hours in atomic-scale resolution. After this time the islands are coalesced together**.**
The mica was modified with ion exchange of Na to Mg by immersion into a Mg-containing solution. Both the modified and unmodified mica has hexagonal packing with 0.58 nm lattice spacing. The modified surface is more advantageous for the adsorption of phosphonate molecules, than the unmodified mica. After 1 day of immersion of modified mica into the phosphonate containing solution, square angle lattice packing of phosphonate molecules were found (Figure 2.).

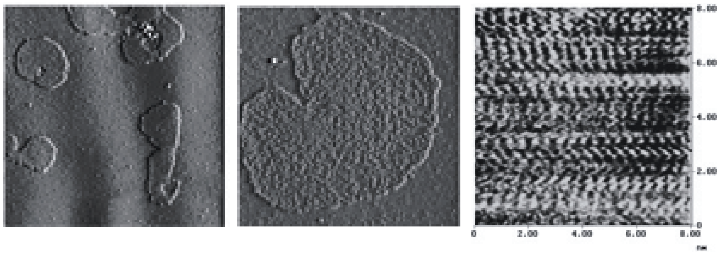

Figure 1. Structure of phosphono-octane layer on mica after a)-b) 18 h and c) 60 h a)4 mikro m b) 1,5 mikro m

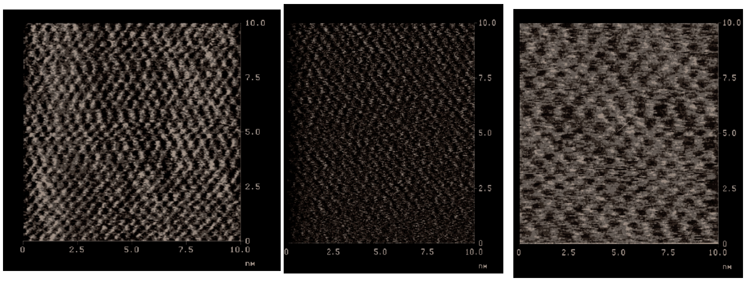

Figure 2. AFM image of the structure of phosphono-octane layer on modified mica surface

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Solvent Electrostriction and Ion Solvation

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Following earlier work of Padova,[1] an expression is developed for the electrostriction of a solvent by the electrical field of an ion per mole of solvent affected by this field. This quantity depends only on the properties of the solvent, and the effects of the charge and size of the ion are taken care of by the solvation number. The operational expression arrived at is:

$$\Delta V_{el}(S) = 2V^*(S)\ \kappa_T(S)\ X / [X^2 - 2(\partial X/\partial P)_T]$$

where $\Delta V_{el}(S)$ is the molar electrostriction of the solvent S, $V^*(S)$ is its molar volume in the bulk, $\kappa_T(S)$ is its isothermal compressibility, and $X = 3(\partial \ln\varepsilon(S)/\partial P)_T - \kappa_T(S)$. The problem is the scarceness of reliable values of the required derivatives, in particular the second pressure derivative of the density and the permittivity. Nevertheless, values were found for several solvents that yielded the following values of $\Delta V_{el}(S)$ /cm^3 mol^{-1}:

water	methanol	1-propanol	Propylene carbonate	4-butyro-lactone	acetonitrile	dimethyl sulfoxide
3.15	5.99	14.41	7.12	9.26	4.93	4.98

among some others.

The electrostriction of the solvent S in the solvation shells of an ion I is the difference between the standard partial molar volume of the ion and its intrinsic volume:

$$\Delta V_{el}(I,S) = V^\infty(I,S) - V_{intr}(I)$$

Ionic values are based on reasonable extra-thermodynamic assumptions, and values of $V^\infty(I,S)$ for aqueous solutions were taken from established sources[2] and for non-aqueous solutions from a recent compilation.[3] The ratio of the solvent electrostriction around an ion and its molar electrostriction is the solvation number of the ion, i.e., the number of solvent molecules in the solvation shells subject to electrostriction:

$$n^\infty = \Delta V_{el}(I,S) / \Delta V_{el}(S)$$

These numbers were obtained for many ions and several solvents and depend mainly on the charges of the ions (but not the sign) and much less on their sizes. The solvation numbers thus obtained are compatible with numbers obtained from other considerations.

When two ions of opposite sign form a contact ion pair some of the solvent molecules in their solvation shells are released to the bulk solvent. The number of molecules thus set free is obtained from the standard molar volume change on ion pairing,[4] obtained in turn from the pressure dependence of the ion pairing association constant:

$$\Delta V^\infty_{ip} = -RT(\partial \ln K_{ip}^\infty / \partial P)_T - \kappa_T(S)$$

where K_{ip}^∞ is the thermodynamic association constant non the molar scale and

$$\Delta n^\infty_{ip} = \Delta V^\infty_{ip} / \Delta V_{el}(S)$$

These numbers of solvent molecules released on ion pairing are comparable with numbers estimated from other considerations.

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Modeling the Polarization of Solvent Molecules

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Intermolecular potential functions that contain terms that describe the polarizability of a molecule are becoming more and more widely used, due to the demand for more accurate models and the availability of computational resources. They are employed in molecular mechanics calculations, molecular dynamics simulations and other force field – based techniques.

It seems, however, that rarely the force field terms that account for polarizability were disentangled from the other constituents of the model and checked independently. Without doing that, the quality of the various methods and of their implementation is difficult to assess. A stringent test for any polarizable model is the polarization caused by the electric field of a neighboring ion.

In an attempt along this line a systematic study[1,2] was performed: We (A) selected the three most widely used methods of describing electronic polarizability: Induced point dipoles, fluctuating charges and the shell model. As molecules that can be polarized, we (B) selected water with its comparatively low polarizability and its high dipole moment and carbon tetrachloride with just the opposite properties. Since the properties of liquid solutions of both substances are of immense biological and technological interest, the results are also important per se. We compared (C) both the induced dipole moment and the interaction energy with the results from accurate quantum chemical calculations that were (D) performed with point charges representing the ion as well as with ‚real‘ ions like Na^+, Be^{2+}, Mg^{2+} and some anions. The dependence of the polarization on the mutual orrientation between ion and solvent molecule was also investigated.

The main conclusions from our work are that the induced dipoles and the shell model perform well (better than the fluctuating charge model), especially for monovalent ions. Divalent ions lead to larger errors in induced dipole moments and interaction energies already at realistic distances from the polarizable molecule.
Besides testing the three models, our study shows from which field-strength onward nonlinear polarizability, inhomogeneous electric fields and overlapping electron densities must be taken into account in polarizable models.

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The Anatomy of Host-Guest Structural Uniqueness by Calorimetry

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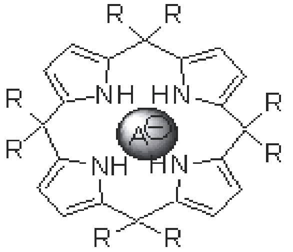
At the present state of the art the design of supramolecular host-guest complexes primarily relies on enthalpic reasoning – the complementarity of the geometric fit, or the charge, or the nature and disposition of certain functional groups. Although it is obvious from fundamental molecular thermodynamics and thus is ubiquitously acknowledged that in addition to enthalpy entropy must play a role in molecular associations, little more than a qualitative statement and the hope that this component will contribute only a minor and to a first approximation negligible share to the overall energetics is included into most constructions of abiotic hosts. One reason for such disregard is the lack of solid quantitative data.



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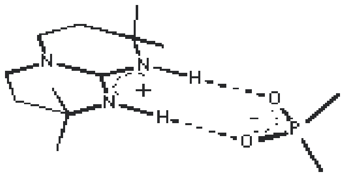

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Calorimetry can fill this gap and may relieve the problem. The systems investigated encompass calixpyrrole 1 and guanidinium 2 anion receptors. They were chosen for the calorimetric dissection of their energetics in host-guest complexations with a variety of anions because of their obvious simplicity which, unlike the much more complex interactions in proteins and other biological receptors, are expected to allow only a quite limited number of explanations of the global energetics. Key to the derivation of the various energetic contributions is the use of trend analyses employing series of similar, yet structurally distinct hosts and guests. Within this ensemble the correlation of the observed increments with the variation in structure allows the sensitive detection of additional interaction modes beyond stoichiometric 1:1 binding (e.g. the formation of higher-order complexes). Furthermore, conclusions on the scope and diversity of host-guest interaction modes are possible. Thus, calorimetry can open the door to judge on structural uniqueness in host-guest complexes. Information on the diversity of binding modes in addition to plain energetics is indispensible for the maximization of binding selectivity and for supramolecular constructions in self-organization and nanotechnology.

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Speciation of Trace Elements in Natural Freshwaters

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A number of trace elements, both essential and non-essential elements, are present at elevated concentrations over the background levels in numerous freshwaters. The impact of metals on aquatic organisms strongly depends on the chemical speciation of the metals.

Speciation of trace metals in natural freshwaters is determined by the interactions of metals with the various ligands, namely inorganic ligands, organic ligands, in particular humic and fulvic acids, organic compounds released by organisms or introduced into water by anthropogenic activities, macromolecules and particles in the colloidal size range, surface functional groups of particles and of organisms. A challenging problem is the study of the interactions of trace metals with natural organic matter.

In our laboratory, we have mostly used two types of techniques to study the interactions of trace metals with natural organic ligands, namely competitive ligand-exchange / adsorption stripping voltammetry or stripping voltammetry (CLE-AdSV or CLE-SV)[1] and diffusion gradients in thin films (DGT).[2,3] Using CLE-AdSV or CLE-SV, a known ligand is added to a natural water sample; after equilibration between the added ligand and the natural ligands is established, the complexes with the added ligand are determined by voltammetry. The free metal ion concentration is then calculated based on the assumed chemical equilibria with the ligands.[1] The DGT technique relies on the diffusion of metal species through a gel layer and yields the concentration of the dynamic (labile and mobile) species of the trace metals.

Cu speciation, as determined by CLE-AdSV, is characterized by strong complexation, presumably by natural organic ligands, in a variety of freshwater environments. Very strong complexation of copper has been observed in eutrophic lakes, where the ratios of free Cu^{2+} to total dissolved Cu are in the order of magnitude $[Cu^{2+}]/Cu(tot) = 10^{-7}$ to 10^{-6}.[1] The dynamic copper species measured by DGT are much higher than the free Cu^{2+}, as they include all labile species which diffuse through the gel.[3] Complexation of Zn is typically much weaker, with ratios of free $[Zn^{2+}]/Zn(tot) = 0.01 – 0.1$. A large part of Zn appears to be labile by DGT.[3] Cadmium is also less strongly complexed than copper. The ratios of $[Cd^{2+}]/Cd(tot)$ in water from eutrophic lakes are in the range 0.01-0.03.[1] A large part of Cd also appears to be labile by DGT. Experimental speciation results for Cu and Zn are compared with modeling of complexation by fulvic and humic acids, using established literature models.[3] These comparisons indicate that stronger complexation of Cu is obtained from the experimental results than expected from binding with fulvic and humic acids. The experimental results for Zn are closer to the modeling results. Implications of these findings with respect to the ligands in natural systems will be discussed.

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Atomistic Simulation of the Structure of Nanomaterials

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A large number of nanoscale materials are known and two elements which form a wide range of representative structures are carbon and gold. Carbon forms fullerenes, carbon nano-tubes,[1] nano-diamond crystals, nano-diamond wires, bucky wires, bucky-diamonds, carbon onions[2] and nano-graphene.[3] Gold forms nanocrystals,[4] nano-rods[5] and hollow structures.[6] The prediction of such structures and the conditions for their stability is an active area of current research. The combination of their small size and the non-equilibrium conditions under which they are formed makes atomic modelling a key element in this area. Being a light element, C based structures may be simulated by means of ab-initio quantum mechanical calculations[2] and we will be show here that such calculations give results which are in very good agreement with experiment.

For Au this direct ab-initio approach is much more difficult. However, methods based on semi-empirical, many-body potentials are an alternative. These potentials are of a form suggested by quantum theory but whose parameters are obtained from a combination of empirical and ab-initio data. We will show that this method when combined with Molecular Dynamics leads to structures of Au nanocrystals and nano-rods in agreement with those observed experimentally.[4,5] Furthermore, simulating heating of these structures is shown to lead to phase transformations which will be important in application of these materials.

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Interaction of Cell-Penetrating Peptide Transportan with Lipid Membranes

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Cell-penetrating peptides (CPPs) are short peptides of less than 30 amino acids that are able to penetrate cell membranes and translocate different cargoes into cells.[1] The only common feature of these peptides (over 100 known today) appears to be that they are amphipathic and net positively charged. The mechanism of cell translocation is not known but it is apparently receptor and energy independent, although, in certain cases, translocation can be partially mediated by endocytosis. One of the efficient CPPs of our interest is transportan (TP), consisting of the active part of neuropeptide galanin attached to mastoparan, the component of wasp venom.[2] TP can enter cells at very low concentrations (nM range) and accumulates mainly in cellular membranes. Penetration of TP into cells is rapid and initially first-order, with half-time of 3.4 minutes at 37°C. Cargoes that are successfully internalized by TP range from small molecules to proteins and supramolecular particles, making TP a promising drug-delivery vector.[3] Most CPPs are inert or have very limited side effects but at higher concentrations TP seems to make pores in the cell membranes.[4] In order to inspect this undesirable action of TP more closely, we prepared giant unilamellar POPC vesicles[5] with entrapped sucrose (0.2 M) or dextrans (1 mM) with or without fluorescein added and transferred single vesicle in the isoosmotic solution of glucose with added TP (1 - 100 μM). The effect of TP on membrane was studied by monitoring the changes of vesicle shape and the transport of small (water, sugars and fluorescein) and large (dextrans) molecules across the membrane. The permeability of the membrane was determined via the time course of halo effect[6] or vesicle internal fluorescence. No effect of TP on the vesicles was detected well below the critical micelle concentration of TP (CMC = 20 μM). Near CMC, the time dependent decrease in the intensity of the fluorescence and brightness of halo was observed. At intermediate TP concentrations (30 - 45 μM) vesicles were destructed. Above 50 μM TP vesicles survived, but the internal fluorescence and halo faded in few seconds. The increase of the membrane surface was also observed. The behavior of vesicles (TP concentration dependent relaxation of membrane tension by the opening of transition tension pores, destruction and final survival of vesicles) was explained in terms of TP induced pores, which size and number was dependent on TP concentration. The model predicts that destruction of a vesicle is possible only when the differences in dimensions of the inner and outer solutes and of their concentrations are large enough. The size of TP induced pores should allow large permeability, but the diameter of pores must still be comparable to the diameter of solute molecules. For the used system (0.2 M sucrose/glucose solution) the diameter of pores between 1.5 nm and 5 nm was assessed. The described system illustrates an interesting specific behavior of peptides dissolved in lipid membranes.

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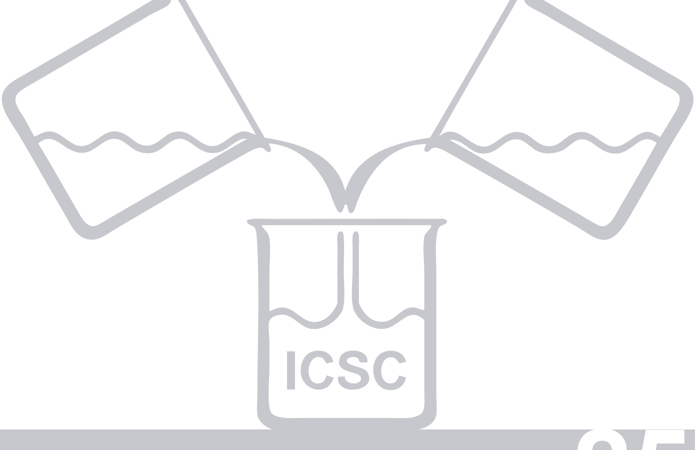
A.
THERMODYNAMICS, KINETICS AND STRUCTURE

Oral Presentations



Bond-Order Analysis of the Mechanism for Proton Mobility in Liquid Water

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Bond order analysis is introduced to facilitate the study of cooperative many-molecule effects on proton mobility in liquid water, as simulated using the multi-state empirical valence-bond (MS-EVB) methodology. We calculate the temperature dependence for proton mobility and the total effective bond-orders (TEBO) in the first two solvation shells surrounding the $H_5O_2^+$ proton-transferring complex. We find that proton-hopping between adjacent water molecules proceeds via this intermediate, but couples to hydrogen-bond dynamics in larger water clusters than previously anticipated. A two-color classification of these hydrogen-bonds leads to an extended mechanism for proton mobility, where "bad" hydrogen-bonds break on the acceptor side whereas "good" ones break on the donor side.

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Volumetric, Vapour Pressure and Electrical Conductivity Studies in Aqueous Solutions with Ascorbate Ions

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Owing to the antioxidant properties, ascorbic acid (Vitamin C) and its salts are used in many clinical applications. Magnesium and calcium ascorbates provide the essential minerals and Vitamin C to the body. The acidic Vitamin C is neutralized and becomes less irritating to the stomach. Ascorbic acid and ascorbates help to improve blood vessel flexibility, aid the metabolism of the amino acids, participate in production of collagen and in many other reactions. Aqueous solutions with ascorbate ions are of considerable interest from biological and chemical points of view and therefore were widely investigated. However, our knowledge about thermodynamic and transport properties of these solutions is less satisfactory.

In this work are presented the volume-concentration-temperature relations in the ascorbic acid-water and magnesium ascorbate-water systems in the 288.15 K to 323.15 K temperature interval. Measured densities permitted to determine the apparent molar volumes, cubic expansion coefficients and other parameters at finite concentrations and at infinite dilution. Vapour pressures of water over saturated solutions of ascorbic acid and calcium ascorbate were measured in the 280.15 K to 319.15 K range and the activities of water, osmotic coefficients and the molar enthalpies of vaporization were derived from them. The limiting ionic conductances of ascorbate ions and the dissociation constants of ascorbic acid were determined from the analysis of electrical conductivities of dilute aqueous solutions of L-ascorbic acid, sodium ascorbate, magnesium ascorbate, calcium ascorbate and ferrous ascorbate.

The obtained results are compared with available in the literature data and discussed with regard to the ion-water and ion-ion interactions.

Towards a Transferable Interaction Model for Water

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We performed molecular dynamics and Monte Carlo simulations for all known crystalline phases of ice, as described by the SPC/E and TIP4P water models. We started from the measured structures, densities and temperatures and carried out classical canonical simulations for all these arrangements. All simulated samples were cooled down close to 0 K to facilitate the comparison with theoretical estimates. We determined internal energies as well as pressures, and monitored how accurately the measured configurations were preserved during the simulations.

We carried out additional simulations to find the best combination of these two potentials, since these two models predict very similar thermophysical and structural properties for water at ambient conditions, but the predicted features for the corresponding ice polymorphs differ significantly. To find the best hybrid interaction model we performed test calculations in the ambient liquid phase as well as we calculated their liquid-vapor phase envelope, vapor pressure and the second virial coefficient. We present the results of our study.

Analytical Theories of Transport in Concentrated Electrolyte Solutions from the MSA

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Ion transport coefficients in electrolyte solutions (e.g. diffusion coefficients or electric conductivity) have been obtained from analytical theories. Such an approach, based on a combination of dynamic theory (Smoluchowski equation) and of the mean spherical approximation (MSA) for the equilibrium pair correlation, allow specific effects of the ions (such as the ion size dependence or the pair association) to be taken into account. The various predicted equilibrium (osmotic pressure and activity coefficients) and transport properties (mutual diffusion, electric conductivity, self-diffusion) are in good agreement with the experimental values up to high concentrations (1-2 mol L^{-1}). Simple analytical expressions are obtained. We discuss the validity of such an approach which is nothing but a coarse-graining procedure.

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Field Theoretical Approach of the Classical Liquids. Application to Ionic Systems.

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We present a simple field theoretical approach of the classical liquids.

The partition function is represented by an integral functional based on a real valued field representing directly the densities. The Hamiltonian of the system introduces the standard interaction potential between particles to couple the fields and a contribution which is simply the ideal gas free energy.

This contribution accounts for the ideal entropy and provides the adequate measure for the fields in order to describe the classical liquid in a way that is equivalent to the standard statistical mechanics for the particles.

This approach illustrates a new way of accounting for the principle of indiscernability of the particles in the case of the fields. Practically, in the perturbative expansion, the coupling terms represent concrete physical effects related with counting properties of the ideal entropy. The pertinence of these terms is illustrated in two examples concerning ionic systems at an interface.

We derive a density profile[1] at the neutral interface consistent with the exact contact theorem, which expresses the mechanical equilibrium at the interface.

The profile results from a coupling between the charge and the density fields, as a consequence that one cannot arbitrarily permute the fields for the cations and the anions in the same way as the standard ideal entropy distinguishes the cation and anion species.

The field theory provides an interpretation of the anomalous behavior of the differential capacitance with the temperature.[2] This effect visible in some experiments and simulations is not accounted for by the popular Gouy-Chapman theory. To our knowledge there is no satisfactory explanation of this phenomenon within the standard approaches.

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Differences between Metal-Ligand Speciation Results Obtained by Electrospray Ionization Mass Spectrometry (ESI-MS) and by "Traditional" Techniques: the Case of Selected Aluminium(III) Systems

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Electrospray ionization mass spectrometry (ESI-MS) is being increasingly applied to study the solution equilibria of metal-ligand systems,[1] together with or in alternative to the techniques traditionally employed to this aim, e.g. potentiometry, UV-Vis, NMR. ESI-MS results are usually different from those obtained by traditional techniques, both in the qualitative (number and stoichiometry of the species observed in solution) and quantitative data (relative concentrations of all species at equilibrium). To our knowledge, a systematic investigation of the nature of these differences and of their causes is lacking in the literature.

In this work, selected aluminium(III)-ligand systems were examined by ESI-MS. The ligands considered were 3-hydroxy-2(1H)-pyridinone, 3,4-dihydroxybenzoic acid, citric acid, and ethylenediaminetetramethylenephosphonic acid. Spectra (in positive and/or in negative ion mode) were obtained at various metal-to-ligand ratios and pH values, and results were compared with those obtained previously [2-5] by traditional techniques.

For the qualitative results, the main differences between ESI-MS and traditional techniques regard the acidic proton content of the metal-ligand species, and the presence of clusters at ES conditions. The former difference is observed when the complexes in solution have acid-base properties and a high charge (> ± 1), and it is due to the easy of the proton displacement at ES conditions. The formation of clusters is an ES artifact which regards polycarboxylic and polyphosphonic ligands, but it can be minimized by strictly optimizing the instrumental parameters. Other minor ES artifacts are the formation of solvent and cation (or anion) adducts, which usually do not impair the qualitative analysis.

For the quantitative results, the differences between ESI-MS and traditional techniques are more evident for the systems which also show significant qualitative differences, and they are due to different solvents and ionic strengths of the solutions analysed, to a different pH definition, and to the presence of ion response factors in ESI-MS.

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Influence of Phase Equilibria on Reaction and Process Design in the Polymer and Chemical Industry

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The knowledge of the solubilities of components taking part in a chemical reaction including the dependence on temperature and pressure is essential for the optimization of chemical reactions. For difficult separations, small uncertainties in phase equilibrium data might have a huge impact on the design of the separation process.[1] Physical property data can be regarded as raw material of chemical process design, where the quality of the raw material might strongly affect the quality of the product. In the presentation examples from industrial practice are given for cases in which solubilities and phase equilibria played and important role to optimize a process or to solve a technical problem:

- Retardation of a chemical reaction due to the high solubility of a reaction product (HCl) in an unreacted educt (alcohol). Measurements of chemical kinetics and of phase equilibria were performed. The productivity could be increased significantly by using a reactive distillation process, which removes the products during the reaction.
- The solubility of a blowing agent (carbon dioxide) in a polyether influences the quality of the rigid polyurethane foam. Phase equilibrium measurements and a modification of the process solved quality problems.
- During the production of polyethers the high solubility of propylene oxide limits the reaction temperature for safety reasons. Phase equilibria of propylene oxide in polyols with different starter alcohols were measured. The influence of the chain length was investigated and a thermodynamic model was developed. The capacity of the plant could be more than doubled.
- In a chemical reaction process a solid intermediate substance occurs. The formation of a solid phase is limiting the conditions for the chemical reaction. Solid-liquid equilibrium measurements under various conditions have been performed. A model describing the phase equilibria taking chemical reactions into account was developed.
- An automated FID alarm indicated very high alcohol contents in the vent line of an aqueous fermentation reactor and led to plant shut downs. Since the alcohol used in the process has a lower vapor pressure than water this behavior was unexpected for the people running the plant. Thermodynamics gives a rather simple explanation.
- Using quantum-chemical and thermodynamic predictive methods in combination with experimental screening methods an entrainer for the separation of isomers in an extractive distillation process was found leading to a reduction of operating costs of some million Euros per year.[2]

Often precise measurements[3,4] of solubilities and phase equilibria are needed to optimize reaction and process design, but sometimes consulting with a sound thermodynamic background is sufficient to solve technical problems.

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On the Use of the Mean Spherical Approximation to Describe Conductivity and Acoustophoresis in Aqueous Media.

I Determination of the Association Constant of Multivalent Salts.

II Determination of the Effective Charge of Nanoparticles.

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The first part of this study deals with the use of conductivity and acoustophoresis experiments on multivalent salts in aqueous media to determine association constants of several multivalent salts: trisodium citrate ($C_6H_5Na_3O_7$), $MgSO_4$ and $MnSO_4$. As we use the mean spherical approximation to describe these two non-equilibrium phenomena (conductivity and acoustophoresis), our description is valid up to an ionic strength of 1 mol/L. Conductivity is usually used to determine association constant of salts but acoustophoresis was never used for this purpose. Our approch gives consistent association constants using both conductivity and acoustophoresis.

The second part deals with the determination of the effective charges of nanocolloids due to ionic condensation of ions on their surface. Two aqueous nanocolloidal suspensions are studied: laponite RD and a spherical magnetite. In the case of conductivity of spherical colloids, the signal Λ is roughly proportional to $\Sigma_i c_i Z_i^2/R_i$, where c_i , Z_i and R_i are respectively the concentration, the algebraic charge and the radius of the species i. Concerning acoustophoresis, the UVP (Ultrasonic Vibration Potential) is proportional to $\Sigma_i c_i Z_i R_i^2$. Usually, for colloidal suspensions, the signal arising from simple ions is negligible in acoustophoresis whereas the signal due to colloids is negligible in conductivity measurements. In the present description, all the charged species are taken into account i.e. the signal that comes from nanocolloids, is not neglected in conductivity and that arising from little ions, is not neglected in acoustophoresis. This approach gives an effective charge of the nanocolloids that consistently reproduce the two experimental results.

Electrostriction Approach to the Debye-Hückel Limiting Law for the Apparent Molar Volumes of Electrolyte Solutions

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In 1941, a paper by Fritz Sauter dealing with the density of dilute strong electrolyte solutions was published in the journal „Zeitschrift für physikalische Chemie“.[1] By using basic results taken from the Debye-Hückel theory, he presented two derivations of the limiting law for the apparent molar volumes (densities) which didn‘t agree with those derived by Redlich and Rosenfeld (RR) by means of the „thermodynamic potential“.[2] The RR limiting laws for density and volumes are considered experimentally verified. In reference a detailed overview can be found.[3]

In this work, the second derivation proposed by Sauter and based on the electrostatic/mechanical treatment of electrostriction (i.e. the change of volume with an electric field) is carefully analysed. As a consequence, a detailed formulation of the thermodynamics of the electrostriction in electrolyte solutions is presented and used in order to get a final agreement with the RR limiting laws. Further applications of the method to other thermodynamic properties will also briefly mentioned.

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OH Vibrational Spectra for the Hydration Shells of Li^+(*aq*) and Al^{3+}(*aq*) Using MD Snapshots in Quantum-Chemical Calculations

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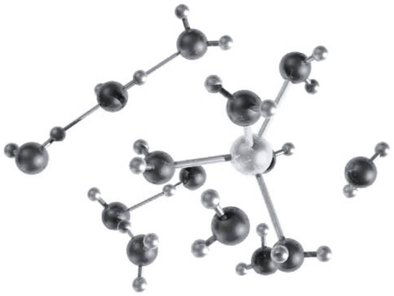
Short- and long-range ion-water and water-water interactions modify both the collective properties of an ionic solution and the properties of the individual solvent molecules in the vicinity of the ion. IR spectroscopic measurements have found that the OH stretching vibrational band for water molecules in the first shell around Al^{3+}(aq) are downshifted by as much as –850 cm^{-1} with respect to the isolated water molecule,[1] but only by some –300 to –400 cm^{-1} around Li^+(aq).[2,3]

Here we present theoretical calculations with a double purpose: to find a good strategy to model $\Delta\nu$(OH) in a solution and to understand the many origins of the $\Delta\nu$(OH).

We present DFT calculations of OH vibrational spectra, using charge-embedded clusters with the geometries taken from snapshots of preceeding MD simulations, which were long NPT simulations using ab-initio derived effective many-body ion-water potentials.[4] In the DFT calculations, both the first hydration shell and part of the second and third shells are included in a supermolecule and more distant molecules are included explicitly as point-charge molecules.

The DFT model, the long-range model, the vibrational model (anharmonic!) and the underlying MD simulation all need to be of a high quality to reproduce the experimentally observed $\Delta\nu$(OH).[5]



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Hydration of Highly Charged Cations and Cation Hydrolysis Effects Studied by Molecular Dynamics Simulations

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A theoretical study of a model of primitive cation M^{Z+} in water has been performed by means of molecular dynamics (MD) simulations in order to clarify the influence of ion charge on hydration structure and dynamical properties of highly charged cations in water. Water is described in the framework of a flexible non-constrained model.

It is shown that a strong cation-water electrostatic interaction leads to a formation of very stable structures constituted preferably by six water molecules, which are octahedrally arranged around a cation. The increase of cation charge and/or decrease of its size results in an increase of OH bond lengths of water molecules in cation hydration shell. Further increase of ion-water electrostatic interaction causes a loss of some protons by hydration shell, which is interpreted as a hydrolysis effect. For correct description of this phenomenon, the considered model is improved by inclusion of effects of charge redistribution between hydrolysis products, which strongly modified the hydrated-hydrolyzed structure of cation decreasing the number of neighbours in first and second hydration shells.

The influence of cation charge on dynamical properties of cation and its hydration shell is also demonstrated. In particular, the value of self-diffusion coefficient of cation essentially decreases with the increase of cation charge, remaining slightly smaller than the one of oxygen of water molecules in first hydration shell. Due to smaller number of neighbours of highly charged cation, the self-diffusion coefficients of oxygens and cation increase with the increase of cation charge. This is a consequence of cation hydrolysis.

For cations M^+ and M^{2+} the spectra of cation and oxygens are characterized by relatively independent movement of cation and water molecules. For highly charged cations a new characteristic common peak in both spectra are observed at high frequencies. This peak is separated from the rest of the spectra, which consists of series of less defined peaks characterizing different types of moves in hydrated-hydrolyzed complex.

Brownian Simulations Contribution to the Study of Particle Dynamics in Solution

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The Brownian dynamics (BD) is a very efficient simulation method to investigate dynamical properties of particles in solution. It treats the solution in the framework of the continuous solvent model and both direct interactions and hydrodynamic interactions between solutes may be taken into account in the calculations. We propose here to show that the BD is adapted to the simulation of various systems.

First, BD allows us to study ionic solutions. The self-diffusion coefficient of each ion and the electrical conductivity of the solution are found in good agreement with experimental determinations in various cases: in aqueous solutions of 1-1 electrolytes as well as in aqueous solutions of micelles. It is shown that hydrodynamic interactions must be taken into account to obtain electrical conductivities in agreement with experiments. The effect of hydrodynamic interactions on the self-diffusion is also striking, especially in solutions of asymmetrical electrolytes: if it remains weak for small ions in 1-10 and 2-20 electrolyte solutions, it is great for macroions in latter solutions (increase of about 15 to 40 %).[1]

On the other hand, non-equilibrium BD is used to calculated the dynamical properties of the electrochemical double layer following an electron transfer. A simple model of an electrochemical cell was developed and the relaxation time of the double layer in 1-1 aqueous solutions was found in the range 0.1 to 0.4 ns for electrolyte concentrations between 0.1 and 1 mol/L and surface charges between 0.032 and 0.128 C m^{-2}.[2]

Finally, BD is also suitable to study real charge-stabilized ferrofluids, with and without the presence of an external magnetic field. The magnetization and birefringence curves are computed, as well as structure factors. It is shown that the microstructure of the ferrofluid becomes anisotropic under the magnetic field.[3]

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Structure of the Liquid-Vapor Interface of Polar Liquids and Their Aqueous Solutions

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Detailed understanding of the molecular level structure of the liquid-vapor interface is of great scientific interest. However, only recently have experimental techniques arrived at the level of sophistication where they can provide meaningful data about such interfaces. This recent development of the experimental methods has also facilitated the computer simulation investigations of such systems.

In this contribution we demonstrate, for the case of liquid water as an example, that confusions in the literature concerning the orientation of the molecules at the interface are originated in the improper statistical treatment often used; an unambiguous description of the orientational statistics of the molecules relative to the interface requires the calculation of the bivariate joint distribution of two independent orientational parameters. Using this method we have found that water molecules have two distinct orientational preferences at the liquid-vapor interface. In the first preferred orientation the plane of the molecule is parallel with the interface, whereas in the second one the molecule is perpendicular to the interface, pointing by one of its O-H bonds straight to the vapor phase. The first of these orientations is present in the entire interfacial region, whereas the second one is only present among the water molecules penetrated farthest into the vapor phase. The two orientations correspond to the alignment of a hydrogen bonded pair of water molecules, in which the molecule located toward the aqueous phase has the first, whereas the one on the vapor side the second of the two preferred orientations.

This analysis is extended to the interface of aqueous solutions of aprotic dipolar as well as hydrogen bonding solutes (e.g., acetone and methanol, respectively) of different compositions. It is found that the presence of a small amount of methanol in the system can already wash out the preference of the water molecules for the second type of orientation, as the methanol molecules can replace these waters by occupying the hydrogen bonding positions at the vapor side of the water molecules aligned in the first of the preferred orientation. In the case of dipolar solutes the orientation of the water molecules is mainly governed by the dipolar forces acting between the water and solute molecules. The study is completed by analyzing the neat liquid-vapor interface of the aprotic dipolar and hydrogen bonding molecules considered.

Hysteretic Behavior on Heat of Protonation of Diethylenetriamine

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Summary**:** Hysteretic behaviour on the heat of protonation of diethylenetriamine (*dien*) was found in aqueous solution. We propose two conformers for H(*dien*)$^+$ to explain an unexpected endothermic spike observed in a protonation process of *dien*. Corresponding two optimized geometries of H(*dien*)$^+$ were given by *ab-initio* MO calculation.

Diethylenetriamine (*dien*) is a simple chain-formed ligand with a backbone consists of only carbons and nitrogens. Protonation constants and enthalpies of *dien* in aqueous solution have been determined by means of potentiometric and calorimetric titration at 298K. Although protonation constants obtained well agree with the literature values, as shown in Fig. 1, a hysteretic behavior on the heat of protonation has been found, *i.e.*, unexpected endothermic spike was observed at the formation of H$_2$(*dien*)$^{2+}$ in the protonation process by HCl titration while the enthalpy profile of deprotonation process of H$_3$(*dien*)$^{3+}$ by NaOH titration was expressed simply in terms of stepwise acid dissociation equilibria as shown in Fig. 1(b). In order to explain this hysteresys, we assumed a presence of two conformers for H(*dien*)$^+$ merely on the protonation process. The solid line in Fig. 1(a) drawn under the following condition: the major (75%) conformer has a larger protonation constant and less negative protonation enthalpy by *ca*. 40 kJ/mol than the remaining (25%) well reproduces the experimental points. However, owing to cancel out of the distribution ratio of the conformers and the respective protonation enthalpies, we cannot determine each value separately.

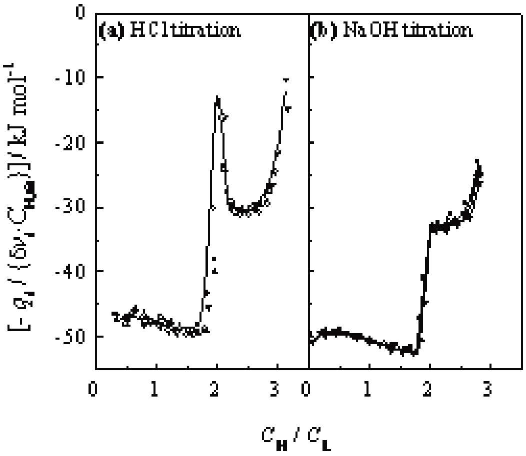

Fig 1: Enthalpic titration curves of diethylenetriamine on protonation (a) and deprotonation (b) processes.

An *ab-initio* MO calculation has been performed for H$_n$(*dien*)$^{n+}$ ($n = 0\sim2$) with 6-311G(d,p) basis functions by using *Gaussian 03* program suite to find at least two stable geometries for H(*dien*)$^+$ as shown in Fig. 2. The '*folded*' form is calculated to be enthalpically more stable by 80 kJ/mol in gases phase than the *'expanded'* form. On addition, owing to the hydrogen bond between the terminal amino groups, the protonation constant of the *'folded'* form is expected to be smaller than that of the *'expanded'* form. We thus concluded them to be the two conformer for H(*dien*)$^+$ found on the protonation process. Because the species H$_2$(*dien*)$^{2+}$ adopts the *'expanded'* geometry predominantly due to the electrostatic repulsion of protonated terminal amino groups, the *'expanded'* H(*dien*)$^+$ was formed merely by the deprotonation of H$_2$(*dien*)$^{2+}$.

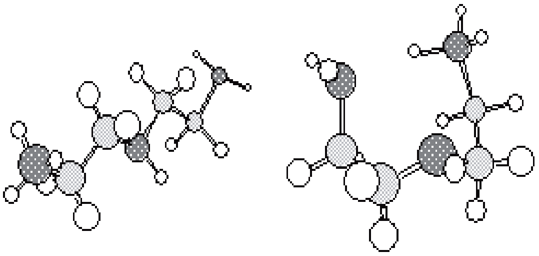

Fig 2: Optimized geometries of 'expanded' form (left) and 'folded' form (right) for H(dien)+.

Hydration of Molecular Anions with Oxygen Sites

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The ion hydration of molecular anions with oxygen sites such as nitrate, perchlorate, and sulphate is of special interest when compared with hydration structures of spherical atomic anions, like the halide anions. The water structure around the different solutes, and their influence on solution properties is discussed in the framework of different simulation methods and integral equation theories. Especially the influence of polarizability of ions and solvent molecules will be discussed.

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Thermodynamic Properties of the Water-Alcanol Solutions of Calcium and Magnesium Chlorides. Experiment and Modelling

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The effect of salts on phase behaviour of water–organic mixtures has found many applications in chemical engineering and there is a great need in systematic experimental data and reliable models describing thermodynamic properties of aqueous-organic electrolyte solutions. Nevertheless until recently these systems were paid only minor attention in comparison with solutions of electrolytes in individual solvents. Over the last decade several thermodynamic models have been proposed to describe phase equilibria in mixed solvent–electrolyte systems. In most works aqueous systems containing alcohols and salts of univalent cations were considered. Phase behaviour of analogous systems with bivalent cations is more complicated partly because in this case the ion hydration and solvation is pronounced much stronger.

In preceding work[1] we developed VLE model for systems containing bivalent cations. Unlike similar models addressing this type of systems that of ours accounted for the hydration and solvation of ions. Activity coefficients of various species (water, alcanol, „free“, hydrated and solvated ions) were described using the UNIQUAC model and the extended form of the Debye-Hückel equation proposed by Pitzer. As is characteristic to other similar models, we made an assumption about complete salt dissociation, independently of composition of mixed solvent and salt concentration.

In this work we present experimental data on the density and electric conductivity of aqueous systems containing 2-propanol or ethanol and calcium chloride or magnesium chloride over a large range of concentrations of the salt and alcanol at 313.15 and 333.15 K. Partial molar volumes of salts in mixtures have been calculated at each temperature. The obtained results give evidence of significant structural variations with the change of the mixed solvent composition. Basing on the electric conductivity data, the thermodynamic constant and the degree of dissociation of calcium and magnesium chlorides in the mixed solvent were calculated. As was anticipated, dissociation of the salt strongly depends on the composition of the mixed solvent. The value of the dissociation constant of calcium chloride turned out to be essentially greater than that of magnesium chloride. This result agrees well with the data on phase equilibria in the considered ternary systems that give evidence of strong interactions between magnesium cation and alcanol molecules.

The VLE model proposed in our previous study was modified by taking into account the dependence of the dissociation degree of calcium and magnesium salts on the composition of the mixed solvent. We infer that the account for partial dissociation of salt in aqueous-organic solvents palpably improves the description of phase equilibria in the range of high alcanol concentrations.

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Coordination Number versus Reactivity – a Heavyweight Fight!

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The chemistry and chemical reactivity of transition metal ions in certain solvents, those that have a bulky structure close to the coordinating atom, is much different than what we normally experience in aqueous media. This is due to the large ligand molecules, which geometrically makes it sterically impossible to let small transition metal ions obtain the coordination number present in aqueous solution.

This study on various transition mteal ions in a series of solvents with different coordination properties is part of a larger investigation of solvated metal ions. It examines the coordination chemistry primarily of the oxygen-donating solvents water, dimethylsulfoxide (DMSO) and the still largely unexplored solvent N,N'-dimethylpropylene urea (DMPU). DMPU is a prime example of a bulky solvent, as it forces many metal ions through sterical hindrance to abandon a higher coordination number for a lower one, which greatly affects their chemical reactivity and crystal formation. In some cases, crystal growth is also severly hampered.

When the octahedral coordination is abandoned for a five-coordinated structure which happens for nickel(II) and iron(III) (and possibly also the other transition metal ions), the chemical reactivity increases dramatically, exemplified with the formation of bromide complexes. On the other hand, when DMPU forces an ion to reduce the coordination to a four-coordinated structure, as for zinc(II), the chemical reactivity drops significantly and no formation of bromide complexes was observed.

Another thorough example used for an in-depth study is being performed the lanthanide series. This survey will uncover the struggle between ionic radius and coordinating capability of DMPU and other similar solvents. However, once coordination alterations have been made, significant changes in the level of the chemical reactivity compared to aqueous systems are almost always noticed.

Hydration Properties of Hydroxy Derivatives of Benzene and Toluene

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A considerable amount of new experimental data has been collected recently on the thermodynamic derivative properties (enthalpy, heat capacity, volume) of dilute aqueous solutions of benzene and toluene and their polar derivative containing OH and NH_2 groups (phenol, cresols, aniline, toluidines, diaminobenzenes, dihydroxibenzenes, aminophenols). These data were obtained over a wide range of temperatures and pressures (up to 350°C and 30 MPa) in a flow mode using the vibrating tube densimetry, and the mixing compensation and the differential heat capacity calorimeters. Most of the references to the instruments used and to the original data sources can be found in two recent articles published in the Journal of Chemical Thermodynamics.[1,2] These results were combined with the data on the Gibbs free energy level (such as the Henry's law constants and aqueous solubilities)[3] in order to perform a simultaneous correlation of the values at the state of infinite dilution as a function of temperature and pressure. A four parameter thermodynamic hydration model inspired by the fluctuation solution theory (FST) was used for this purpose. The main objective was to establish group contribution functions for the OH and NH_2 groups compatible with the group contribution scheme proposed earlier for hydrocarbons.[4]

Aknowledgement. This work has been performed in connection with a new data project (2005 – 2007) on hydration properties of organic nonelectrolytes supported by IUPAC and IAPWS (http://www.iupac.org/projects/2004/2004-036-1-100.html).

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Ionic Strength Dependence Patterns for Mo(VI)-EDDA, Mo(VI)-IDA and W(VI)-IDA Complexes in Different Sodium Perchlorate Aqueous Solutions

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The equilibria in Mo(VI)-EDDA, Mo(VI)-IDA and W(VI)-IDA systems have been studied in aqueous solution. Stoichiometry and stability constants of the complexes formed are determined from a combination of potentiometric and Uv spectroscopic measurements based on the continuous variations method. All measurements have been carried out at 25 °C and different ionic strengths ranging from (0.1 to 1.0) mol/L ($NaClO_4$). In W(VI)-IDA system the pH was justified to 7.5 but in the other complex formation reactions the pH was fixed at 6.0. According to these results the metal to ligand ratio is 1:1 with the general formula (MO_3L^{2-}, M = Mo(VI) or W(VI)).

The stability constants have been caculated using Microsoft Excel 2000 program. Three empirical parameters C, D and E have been used in a modified Debye-Huckel equation in order to obtain better consistency between the experimental and calculated results. The Solver, Microsoft Excel 2000 powerful optimization package, has been used to perform non-linear least-squares curve fitting. In all complex formation reactions high values of correlation coefficients have been obtained. Comparisons are made of chelate stability constants at different ionic strengths. There are same ionic strength dependence patterns for Mo(VI)-IDA and W(VI)-IDA systems but there is a different pattern for Mo(VI)-EDDA. Ultimately we have looked for a relation between structure of these complexes and the ionic strength dependence pattern.[1-6]

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Diethylsulfoxide *vs.* Dimethylsulfoxide: Peculiarities and Applications

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Our systematic studies on solutios of diethylsulfoxide (DESO), the nearest homologue of DMSO, reveal new physicochemical features, which early have not been reported.[1-4] Moreover, DESO has already received worthy biomedical applications: in some cases even are more pronounced compare with DMSO.[5,6] The several important physicochemical characteristics of DESO including aqueous solutions have been verified and first reported: melting point of pure substance,[3] density,[1] dielectric relaxation data,[2] vapor pressure,[3] and volumetric properties.[1]

Analysis of the complete vibrational spectra also leads to the conclusion that very strong interactions take place between DESO and water, even stronger than those between DMSO and water.[4] The simultaneous existence of strong DESO-H_2O and DESO-DESO interactions suggest the coexistence of many types of structural molecular aggregates, the presence of which plays a significant role also in diluted water solutions. Our recent investigations have shown that DESO + water system could provide amorphous, glassy systems, thus avoiding ice crystallization, in a wide range of concentrations and even at very low cooling rates. The ability of DESO to act as an effective cryoprotectant on E. coli survival was also studied and compared with other commonly used cryoprotective agents. The results also confirm that DESO, more than DMSO, is able to penetrate living tissues without causing significant damage.[6]

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Study of a Binary Critical Mixture of Methanol-Hexane: Measurements Specific Heat, Dynamic Light Scattering and Ultrasonic Attenuation

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Dynamic light scattering measured for the system methanol-hexane to determine critical amplitude ω_0 of the characteristic frequency to scale ultrasound attenuation data. It is found $\omega_0 = 44\times10^9$ s^{-1} and $\xi_0 = 3.2\times10^{-10}$ m. The sound attenuation coefficient was measured between 0.2 and 200 MHz as a function of frequency at various temperatures near the critical.

The relaxation rates of order parameter fluctuations, as resulting from the acoustical spectra, within the limits of experimental error agree with those from a combined evaluation of the lights scattering and shear viscosity measurements.

Measurements of the temperature dependence of the specific heat capacity at constant pressure lead to the critical amplitude $A=6.99\times10^{-2}$ J/(cm^{3}K). The two-scale factor universality is tested by combining the values of ξ_0 and A.

Excess Properties of Aqueous Mixtures of Methanol: Realistic and Primitive Models

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The water + methanol binary systems have attracted a good deal of attention of scientific community due to an unusual non-ideal behavior showed by their excess properties.[1] Neutron scattering experiments shows that these mixtures exhibit extended structures in solution despite the components being fully miscible in all proportions. In the composition interval between methanol mole fraction 0.27 and 0.54 both methanol and water appear to form separate, percolating networks.[2] In alcohol concentrated aqueous mixture, anomaly arises from an incomplete mixing and from retention of remnants of the three dimensional hydrogen-bonded network structure of bulk water.[3]

In this work, extensive NpT Monte Carlo simulations at 0.1 MPa, and 298.15 K have been performed for methanol and water and their mixtures with compositions covering the whole composition range. Both realistic intermolecular potentials and primitive models (i.e., models descending directly from the considered parent models) have been considered. From these simulations, excess and partial molar properties are obtained. In addition, NVT simulations at the corresponding densities have been performed to calculate the site–site radial distribution functions and carry out a cluster analysis.

Whereas the excess properties obtained form realistic models agree quite well with experimental data, this is not the case of partial molar quantities. The obtained results clearly show that the realistic potentials are not able to reproduce, even qualitatively, the experimentally observed minima. The same then applies, evidently, to primitive models that closely follow the results of the parent realistic models. Structural properties, particularly with emphasis on the concentration ends, are then also shortly discussed.

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Anomaly of the Basicity of Water in Mixed Solvents

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In the course of studies on preferential solvation of Co(II) ions in water (Gutmann's donor number, D_N = 18) with formamide (FA; D_N = 24), N-methylformamide (NMF; D_N = 27) and N,N-dimethylformamide (DMF; D_N = 26.6),[1] it was found that FA and NMF were preferentially solvated with the Co(II) ion over water at all concentrations, but that in the DMF-water system, DMF was preferentially solvated with the cobalt(II) ion at low concentrations of DMF, while water became preferentially solvated at the high concentrations of DMF. The isosolvation point appeared at the mole fraction of DMF, $x_{DMF} = 0.6$. This result suggested that the basicity of water toward the Co(II) ion increases (or the basicity of DMF decreases) at high concentrations of DMF. It has been sometimes suggested that the donor number of water is not 18 but it should be about 30. In some books the donor number of methanol (D_N = 19.0), and ethanol (D_N = 20) are given as 30 and 32, respectively.[2]

Raman spectroscopic measurements in DMF-H_2O mixtures showed that the O-H frequency of water increased with the concentration of DMF, while no increase in the O-H frequency could be observed in water-FA and water-NMF mixtures.

Solution X-ray diffraction measurements have been made for various DMF-H_2O mixtures, and significant intermolecular interactions between DMF and water molecules in solution have been observed. The composition and the structure of DMF-water associates are being investigated.

The partial charges of the oxygen and hydrogen atoms of water and DMF molecules were calculated by using a variety of population analysis methods and basis sets for various water-DMF associates. No significant increase was found in the partial charge on the oxygen atom of water at the formation of DMF-H_2O and DMF-HOH-DMF associates compared with H_2O-HOH, H_2O-HOH-OH_2, and $(H_2O)_5$ oligomers, but a three dimensional electron density map showed that more electrons are transferred to the H_2O molecule in DMF-HOH-DMF than to the central water molecule in H_2O-H_2O-H_2O. The gas-phase proton affinity was found to be 993.32 kJ mol^{-1} in the DMF-HOH-DMF associate compared with 883.41 kJ mol^{-1} in the H_2O-HOH-OH_2.[3]

The anomalous behavior in the basicity of water will be discussed.

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Coordination Chemistry of d^{10} Metal Ions in Liquid and Aqueous Ammonia

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The structures of the ammonia solvated d^{10} metal ions have been determined in liquid and aqueous ammonia solution by means of EXAFS and in the solid state by means of crystallography. The ammonia solvated copper(I), silver(I) and gold(I) ions are two-coordinated in linear fashion in aqueous ammonia.[1,2] On the other hand, the copper(I) and silver(I) ions are triangular liquid ammonia, while the gold(I) ion remains two-coordinated. The ammonia solvated zinc(II), cadmium(II), mercury(II), indium(III) and thallium(III) ions are tetrahedral, octahedral, distorted tetrahedral, octahedral and octahedral, respectively, in both liquid and aqueous ammonia.[2] An overview of the structures of the ammonia solvated d^{10} metal ions in both liquid and aqueous ammonia will be given, and the reasons for the different configurations of the copper(I) and silver(I) ions in liquid and aqueous ammonia solution will be discussed.

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Elasticity of Spatial Network of Hydrogen Bonds in Liquids and Solutions

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The elasticity of the spatial network of H-bonds manifests itself in the tendency of the network to retain its initial configuration.[1] This property of the network responsible for such effects in solutions as hydrophobic interactions, microstratification on H-bond network and microheterogeneity of diluted solutions of non-electrolytes in solvents with spatial H-bond network.

How can the elasticity of the network of hydrogen bonds be characterized? The elasticity of H-bonds spatial network of a liquid is discribed most adequately by the isothermal compressibility $\beta_T = -1/V(\Delta V/\Delta P)_T$ or by the module of all-round compression $\mathrm{K} = 1/\beta_T$.

Using a specially designed direct-compression instrument,[2] we measured the isothermal compressibility of three classes of solvents: diamines, diols and aminoalcohols and also light and heavy water - the liquids with the spatial H-bond network, and calculated elasticity of the studied liquids at 298K ($\mathrm{K} = 1/\beta_T$). We compared elastic properties of solvents with spatial H-bond network and with liquids without it, namely, liquid alcanes, aliphatic alcohols, benzene, carbon tetrachloride and tetramethylurea. The elasticity of solvents with the spatial H-bond network is four times higher than that for alcanes and twice as high as that for aliphatic alcohols. Besides, its dependence on the length of hydrocarbon chain in molecule is different. This analys is led us to conclusion that the elasticity of water, diamine, diols and aminoalcohols should be attributed to the elasticity of the H-bond spatial network.

The elasticity of H-bond spatial network of aqueous solutions of diamines, diols and aminoalcohols was studied also. The region of the maximum of elasticity of the mixed H-bonds network was revealed for the each studied systems.

Two opposite proceses take place in the studied solutions: on one hand - the fixing of the network due to the water - non-electrolyte interactions and on other hand - the increase of the mixed H-bonds network defects due to the carbonhydrogen bridges in non-electrolyte molecules.

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Solvation of Tetreaalkylammonium Chlorides in Acetonitrile-Water Mixtures: Mass Spectrometry of Clusters and Molecular Dynamics Simulations

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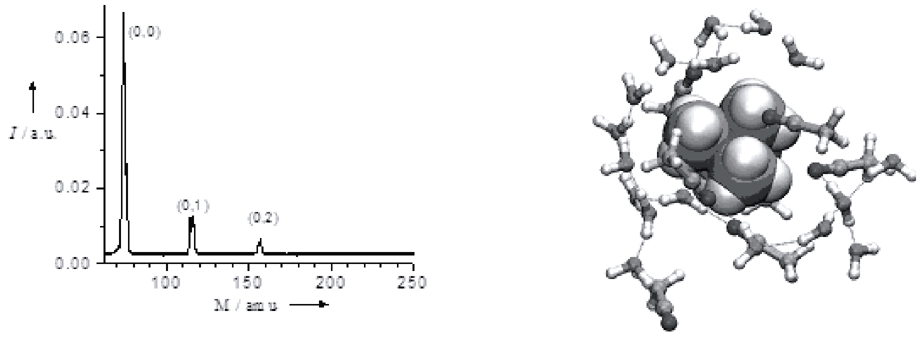
The solvation of tetramethylammonium chloride (Me_4NCl) and n-tetrabutylammonium chloride (Bu_4NCl) in water/acetonitrile mixtures was investigated by means of mass spectrometry of clusters isolated from the solution.[1] As far as the positive ions are concerned, clusters composed of alkylammonium ion and acetonitrile molecules only were observed, even for mixtures with high water content, as shown in the Figure (a); for the negative ions, instead, clusters composed of chloride with both water and/or acetonitrile molecules were observed. For the smaller system (Me_4NCl) we have run quantum chemical calculations and molecular dynamics simulations. It was found that, even though water is present in the solvation shell of Me_4N^+, only acetonitrile has a strong electrostatic interaction with the cation. Water molecules around Me_4N^+ form hydrogen bonds with other water molecules and they interact with Me_4N^+ mainly via dispersive interactions. In Figure (b) we show a snapshot obtained from the MD simulation where such a cage of hydrogen bonded water molecules is evident. These results indicate that Me_4N^+ behaves like a hydrophobic solute. On the other hand, the interaction of Cl^- with water and acetonitrile is of comparable strength and in both cases the electrostatic interaction is dominating. This work demonstrates, experimentally and theoretically, that positive and negative ions give rise to characteristic solvation structures in mixed solvents: even a relatively small organic cation such as Me_4N^+ exhibits a hydrophobic-like solvation shell.Figure: a) the mass spectrum (positive detection mode) of a solution 10^{-3} M of Me_4NCl in water/acetonitrile mixture; (n,m) labels refer to $Me_4N^+(H_2O)_n(CH_3CN)_m$ peaks; b) a snapshot obtained from MD simulation of tetramethylammonium ion in water/acetonitrile mixture showing Me_4N^+ with its first solvation shell.



a)

b)

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An Improved Version of a Transferable Analytical Potential for Water

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The theoretical study of the solvation of ions is important not only for its intrinsic value in physical chemistry, but also to gain insight into various phenomena such as ion selectivity and water exchange mechanisms.[1] The difficulties to obtain reliable experimental data for individual ions hinder the use of effective empirical models; instead, models of solvent molecules are needed that can respond to the strong interactions with the ions[2] and whose parameters are fitted to ab initio calculations and gas-phase experimental data.[1] This latter is the case of our MCDHO model for water[3] that during the last years has been tested in its ability to accurately describe various phases, from the gas[3] to the liquid[4,5] and the solid,[6] and even under supercritical conditions.[7] Four major limitations have been detected: (1) very large quantum corrections that cause an excessive loss of structure in the liquid;[8] (2) very slow dynamics;[4] (3) a too high static dielectric constant for the liquid,[5] and (4) a polarization catastrophe for highly charged cations.

A revision of the possible causes of these limitations resulted in the reparametrization of the MCDHO model presented here that yields a much better agreement with the structural, dielectric and dynamic experimental data of liquid water, at the cost of a somewhat worse description of small clusters and ice Ih. Though this reparametrized model performs well, a discussion of further improvements is also presented.

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Molecular Dynamics Simulations of the Solvation of Lithium, Sodium, and Silver Ions in Acetonitrile/Water Mixtures

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Acetonitrile/water mixtures phase separate into acetonitrile-rich and water-rich regions below 272 K at a molar fraction of 64% water. Above this critical point, the mixture experiences microheterogeneity, i.e. acetonitrile-rich clusters are intermixed with water-rich clusters. The upper critical solution temperature is changed by dissolution of different salts in the mixture. Homoselective solvation decreases the stability of the mixture, while heteroselective solvation increases the stability. For instance, $AgNO_3$ is known to increase the stability of the mixture, while $NaNO_3$ is known to decrease it. Most metal ions, such as Li^+ and Na^+ ions, are better solvated by water than by acetonitrile, while the monovalent coinage metal ions, such as Ag^+, are better solvated by acetonitrile than by water.

New analytical model potentials were developed from ab initio calculations, to gain further insight into the solvation of Li^+, Na^+, and Ag^+ ions in water/acetonitrile mixtures. For each ion, the interaction energies for a large number of ion-solvent clusters were computed at the MP2/triple-zeta level, and the resulting potential surface was fitted to analytical potential functions. The solvent-ion interaction for the Li^+ and Na^+ ions was found to be adequately described using a pair + polarizable model, while for the interaction with Ag^+, due to the additional covalent contributions, additional three and four-body terms were necessary.

Molecular dynamics simulations of Li^+ and Na^+ ions dissolved in the pure solvents and in mixtures of acetonitrile and water, using these new model potentials, were subsequently performed. The Li^+ ion was found to be tetrahedrally coordinated in all mixtures, while the coordination geometries for Na^+ and Ag^+ were found to vary considerably. The Na^+ and Ag^+ ions are on average surrounded by 5-6, and 4-5 solvent molecules, respectively. It was indeed found that the Li^+ and Na^+ ions are preferentially solvated by water, while the Ag^+ ion is preferentially solvated by acetonitrile.

Salt-Induced Phase Separation of Acetonitrile-Water Mixtures

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Acetonitrile is miscible with water at any ratio when temperature is 25 °C. However, acetonitrile-water mixtures are separated into acetonitrile-rich and water-rich phases by either cooling or addition of salt, such as NaCl. Various physicochemical properties, such as viscosity and self-diffusion coefficient,[1] have been measured to elucidate phase separation of acetonitrile-water mixtures. However, the mechanism of phase separation of acetonitrile-water mixtures has not yet been well understood at the molecular level. Our previous investigation on NaCl-induced phase separation of acetonitrile-water mixtures by small-angle neutron scattering (SANS) and large-angle X-ray scattering (LAXS) techniques has shown that phase separation of acetonitrile-water mixtures occurs by the following process.[2] (1) Acetonitrile and water molecules are inhomogeneously mixed at the molecular level, thus, both acetonitrile clusters and water clusters coexist in acetonitrile-water mixtures; (2) when NaCl is added into acetonitrile-water mixtures, Na^+ and Cl^- are preferentially solvated by water molecules; (3) hence, water clusters are gradually evolved around ions with increasing salt concentration; (4) finally, phase separation occurs when water clusters are evolved to a macroscopic scale.

In the present investigation, to compare phase separation of acetonitrile-water mixtures by addition of alkali chlorides, LiCl, NaCl, and KCl at the molecular level, SANS, NMR relaxation, and LAXS experiments at 25 °C have been made on acetonitrile-water-alkali chloride mixtures before phase separation. Phase diagrams at 25 °C obtained in the present investigation showed that phase separation of acetonitrile-water mixtures takes place at lower salt concentration in the sequence of NaCl < KCl < LiCl, although enthalpy of hydration for the alkali ions is smaller in the sequence of $Li^+ < Na^+ < K^+$. The LAXS results revealed that hydrated ions increase in the mixtures with increasing salt concentration, and the results of NMR relaxation showed that the rotational motion of water molecules in the mixtures is more strongly restricted by hydration of ions in the sequence of $Li^+ > Na^+ > K^+$. These findings are consistent with the magnitude of hydration for the alkali ions, but not the sequence of phase separation. The SANS results showed that water clusters are more easily enhanced with increasing salt concentration in the same sequence as phase separation. On the basis of all the present results, the mechanism of alkali chlorides-induced phase separation of acetonitrile-water mixtures will be discussed at the molecular level.

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Pair Potentials from Diffraction Data: a Neural Network Solution

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The inverse theorem of liquids states a one to one correspondence of classical mechanical pair potentials and pair-correlation functions. It holds, if the system is in equilibrium and the internal energy is a sum of pair-wise additive potentials. The relation can be extended to the structure factor that is the Fourier transform of the pair-correlation function and can be determined experimentally. The classical mechanical simulations (molecular dynamics and Monte Carlo simulation) provide the exact pair-correlation functions, if one starts from known pair interactions. There is no exact method in the opposite direction, when the pair-interactions are the unknowns and the pair-correlation functions are known a priori. The early attempts use the integral equation theory of liquids and closure relations are used, like the Percus-Yevick or the Hypernetted Chain ones. There is also a combination of the reverse Monte Carlo simulation and the Born-Green-Yvon hierarchy. Nowadays, iterative simulation methods are preferred, where the pair interactions of the systems are modified systematically in each step as long as the experimental data are reproduced.

In this study, we applied neural networks to get pair interactions form known structure factors. Neural networks have nothing to do with physics and can be interpreted as a non-linear mathematical method to approximate functions or functionals. We performed 700 molecular dynamic simulations on one-component systems with different potentials and the structure factors were calculated. 600 of the pair interaction – structure factor pairs were applied to optimize the weights of the neural network. The performance of the method was tested on the other 100 simulations.

The method provides reasonable potentials for the most of the systems or at least good guesses as a starting potential of an iterative process. The extension of the training data set and an open server version of the method are in progress.

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NMR Studies of Some Metal Ion – Ligand Systems: Equilibrium, Structure and Dynamics

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According to our knowledge the NMR Spectroscopy is the most widely used experimental method in chemistry research including the field of metal-complexes. Using the vastly different NMR technics (often developed for organic chemistry) many questions raised in preparation and characterisation of metal-ligand coordination compounds can be answered. Several aspects of such kind of science are: equilibrium constants, the stoichiometry of species including solvation, constitution, i.e. binding mode and denticity of a ligand, isomers, rate of the formation, ligand exchange reactions, fluxionality etc. Selected examples mainly from our own experimental work done in the last decade are going to be presented. Without the technical details we try to show the advantages and limitations of the multinuclear 1D and 2D NMR spectroscopy in coordination chemistry.

Although NMR does not usually have the precision of potentiometric measurements in order to determine the stability constants, it can provide an important independent check on their accuracy, e.g. Al(III) – F^- system.[1] Combination of the two methods can provide complete speciation of very complicated systems, e.g. Mo(VI) – H^+ – H_2O_2 – SO_4^{2-} – PO_4^{3-} system.[2]

High resolution NMR spectroscopy is superior to study the structure of complexes in solution, but there is an obvious need to take into account the intra molecular isomerisation / fluxionality of the complexes, because a fast rearrangement of the donor atoms (including the water) in the inner sphere might virtually increase the symmetry. Examples of metal-metal bonded cyanides, $(CN)_5Pt\text{-}Tl(CN)_n^{n-}$ (n=0,1,2,3)[3] for symmetry, whilst Al(III)-citrate[4] for fluxionality will be mentioned.

Ligand exchange reactions can also be studied by NMR using the line shape analysis (T_2 time scale) or the magnetisation transfer methods (T_1 time scale, selective MT or 2D EXSY). Selected examples include U(VI)- carbonate[5] and Tl(III) – cyanide[6] systems.

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Thermodynamics of Real Media: A Nonextensive Approach

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The reactivity of some systems does not comply with strict requirements of the classical thermodynamics, especially when the affinity depends on the system mass. This is the case of numerous dispersed „nano-phases" in liquids (such as micelles, microemulsions), of substrats of nanometric sizes (nano-materials, nano-porous), of interpenetrated domains (bicontinuous media), or natural compounds such as humic acids. This means that for all these systems the fundamental properties of extensivity of the function of state is not respected. Then, it is logical to try to explore in the mass of thermodynamic approaches a way which does not impose the extensivity. Physicists[1-3] have shown that it is possible to extend the applications field of thermodynamics to this kind of problem by using nonextensive state functions. Thus, by a statistical approach, C. Tsallis[3-4] proposed a nonextensive form of the entropy which involves a fractal dimension. Although the suggested functions are interesting from a fundamental point of view, they are often difficult for the chemist to exploit. Therefore, we have attempted to tackle this problem in another way, and propose a generalization of the rules of classical thermodynamics so that they can be adapted to the description of chemical reactivity in complex media. Thus, to allow the state functions to have the possibility of being or not being extensive, we propose to assume that the state functions can be Euler's functions of the system mass with a homogeneity order, m, other than one. For m = 1, the rules of classical thermodynamics apply. The state functions will be named „superextensive" for m > 1, and „subextensive" for m < 1. We describe the justification and consequences of these conventions and their application to chemical reactivity. The rule of additivity of the nonextensive entropy obtained by our approach is similar to that proposed by C. Tsallis.

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Solvation Thermodynamics of Hydrophobic Solutes in Water/Cosolvent Systems: Driving Forces for Preferential Solute-Cosolvent Interactions Inferred from Detailed Atomistic Molecular Dynamics Simulations

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Entropy changes are important driving forces in many molecular association processes in chemistry and biology. In my contribution, I will discuss how one may better understand how entropy drives the "preferred binding" between a hydrophobic solute (methane) and cosolvent molecules in aqueous solution mixtures.[1,2] Preferential solute-cosolvent interactions occur when the methane solvation free energy decreases with the cosolvent concentration, whereas preferential "wetting" of the solute occurs when the free energy increases. It is a common practise to reach conclusions regarding the driving force and mechanism for interactions in aqueous solution from observed enthalpies and entropies of interaction. As has been realized for long time, this procedure is frequently unjustified: mutually compensating changes in enthalpy and entropy, which are often ascribed to changes in solvent "structure", frequently occur in aqueous solution with small changes in free energy.[3] I will emphasize the solvation entropy having a contribution that arises from fluctuations of the solute-solvent interaction energy ("fluctuation entropy" or "solute-solvent entropy") as well as having a contribution arising from the energy dissipated in reorganizing the solvent locally ("the solvent reorganization energy"). While the first entropy contribution affects the free energy change, the second does not because it always cancels against a similar contribution present in the solvation enthalpy (exact energy-entropy compensation). Hence, driving forces for preferential interactions can be understood better when interpretations are based on analyses of the fluctuation entropy and solute-solvent energy while disregarding energetic components related to changes of solvent "structure". We performed detailed atomistic molecular dynamics simulations and calculated all above-mentioned thermodynamic quantities in several binary solvents. I will present results for ionic and non-ionic aqueous solutions (cosolvents: NaCl, urea, DMSO, acetone, tert-butanol). The molecular driving forces responsible for preferential solute-cosolvent interactions observed in DMSO/H_2O, acetone/H_2O, and tert-butanol/H_2O and preferential solute-water interactions observed in NaCl/H_2O and urea/H_2O will be discussed. It will be shown that the fluctuation entropy opposes preferential solute-cosolvent interactions in systems where the cosolvent-water interaction is strongly attractive relative to water-water interactions (NaCl, urea, DMSO) while favouring solute-cosolvent interactions in systems where the cosolvent-water interaction is weaker (acetone, tert-butanol). This analysis allows interpreting free energy changes based upon the energetic nature of solvent-solvent and solute-solvent interactions and should benefit the establishment of relationships between the chemical nature of the cosolvent and free energy changes of nonpolar solvation.

The constant-pressure solvation enthalpy, entropy, and solvent reorganization energy, despite being notoriously difficult to obtain in molecular simulations with sufficient statistical accuracy, were calculated too. We find that the solvent reorganization energy and solvent internal pressure ($T\alpha_p/\kappa_T$) depend on the cosolvent mole fraction of solution in a similar fashion. Estimates of the solvent reorganization energy based on the simple relation $(\Delta U_{reo})_P = T\Delta V\alpha_p/\kappa_T$ reproduce the values obtained in the exact calculations within 10%. It will be shown that maxima observed in the compositional dependencies of the internal pressures as well as the methane solvation enthalpies and entropies in the various systems coincide with extremes in solution structure. Although, in the water-rich region of all systems studied, solvation entropies (and enthalpies) are increasing functions of cosolvent concentration, the driving force for preferential methane-cosolvent interaction need not be the entropy gain: In DMSO/water, preferential methane-DMSO interactions are driven by the methane-DMSO dispersion energy while being opposed by the fluctuation entropy. A similar behaviour is observed in solvating larger aliphatic hydrocarbons in aqueous urea solution.[4]

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Comparison of Electrolyte and Non-Electrolyte Solvation in Aqueous Alcohol Mixtures

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Understanding the thermodynamics of solvation in mixed aqueous solvents is one of the classical problems in solution chemistry. While it has been possible to account quantitatively for the solvation of both simple electrolytes and non-electrolytes in purely non-aqueous mixed solvents,[1] the same is not true for aqueous mixtures where success has been more variable.

Solvation in mixed solvents has, to a degree, treated electrolytes and non-electrolytes separately, with different theories being applied to each. In part this reflects the marked differences in the energetics of the solute – solvent interactions; thus, those for simple electrolytes are hundreds of kJmol^{-1}, comparable to covalent bonds, while those for non-electrolytes are about a tenth as strong. Nevertheless, the interactions are qualitatively similar and a theory of solvation should account for both types of solute.

In the case of randomly solvated solutes, simple relationships are expected between the enthalpy and entropy of transfer of the solute and the excess enthalpy and entropy of mixing of the mixed solvent.[1-3] There is good reason to believe that simple electrolytes are randomly, or nearly randomly, solvated in aqueous – alcohol mixtures. Thus it is interesting to compare the thermodynamics of solvation of simple electrolytes and non-electrolytes in these solvent systems.

In the present paper we report transfer free energies, enthalpies and entropies for acetonitrile, as a representative non-electrolyte, in aqueous alcohol mixed solvents. These data, along with comparable literature data for simple electrolytes are analysed in terms of the simple solvation model.

It is found that the model sensibly accounts for the solvation of simple electrolytes across the whole range of solvent compositions, but that the values for acetonitrile systematically diverge from the predictions at higher alcohol concentrations, the concentration at which deviations are observed becoming lower for larger alcohols.

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Molecular Self-Association Assisted by Solvent: Microheterogeneity Inherent in Binary Mixed Solutions

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The self-association of organic molecules in water is well-known behaviour as ‘hydrophobic effect’. However, we have observed that an alcohol forms hydrogen-bonded self-association clusters even in some organic solvent.[1] This suggests that a large hydrogen-bonding network of water is not indispensable for forming molecular self-association clusters. Here we would like to present the mechanism for this molecular self-association in binary mixed solutions, on the basis of the mass spectrometric analysis of clusters isolated from solutions.

The clusters forming through relatively strong interactions such as hydrogen-bonding, dipole-dipole, electrostatic interaction, etc. in a solution were isolated from fragmentation of liquid droplets via adiabatic expansion in a vacuum system. The resulting clusters were analyzed by a quadrupole mass filter (Extrel C50).

By this mass spectrometry, we measured molecular clustering of 1-butanol or 1-pentanol in various solvents: water, methanol, ethanol, 1-propanol, 1,2-dichloromethane and 1,2-dichloroethane. In 1-butanol and in 1-pentanol, saturated by water, the alcohol self-association clusters were formed through hydrogen-bonding interaction, but hydrogen-bonded water clusters were not formed. In pure 1-butanol and in pure 1-pentanol, without adding water, any alcohol self-association clusters were not formed. This alcohol self-association is obviously promoted by the presence of water, but it looks like independent of the hydrogen-bonding network of water.

The self-association of 1-pentanol was also promoted by the mixing with methanol or 1,2-dichloromethane, but not by the mixing with 1-propanol or 1,2-dichloroethane. This shows that the molecular self-association is controlled by the size of solvent.

In comparison with pure 1-butanol and pure 1-pentanol, the stabilization energies of 1-butanol and 1-pentanol should be reduced by the contact with the relatively small molecules such as water, methanol and 1,2-dichloromethane. In order to complement the loss of the stabilization energy, 1-butanol and 1-pentanol would form the hydrogen-bonded self-association clusters. Such promotion of the microheterogeneity should be inherent in binary mixed solution, but not a matter of peculiar behaviour in water.

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Aqueous Interfaces with "Hydrophobic" Room Temperature Ionic Liquids. A Molecular Dynamics Study

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We report molecular dynamics studies on the aqueous interfaces with „water immiscible“ room-temperature ionic liquids „ILs“ based on alkyl-substituted imidazolium$^+$ cations and PF_6^- anions. The neat interfaces are compared with the [BMI][PF_6] versus [OMI][PF_6] ILs, demonstrating the importance of N-alkyl susbtituent (Butyl versus Octyl, respectively) on the extent of solvent mixing, on the polarity and nature of the interface (Figure). The influence of water model is discussed. The results obtained at preformed interfaces are compared with those obtained from mixing - demixing computer experiments.

Comparison of these results with those obtained at aqueous interfaces with classical organic solvents (e.g. chloroform) allows us to better understand the specificity of the interfaces with ionic liquids.

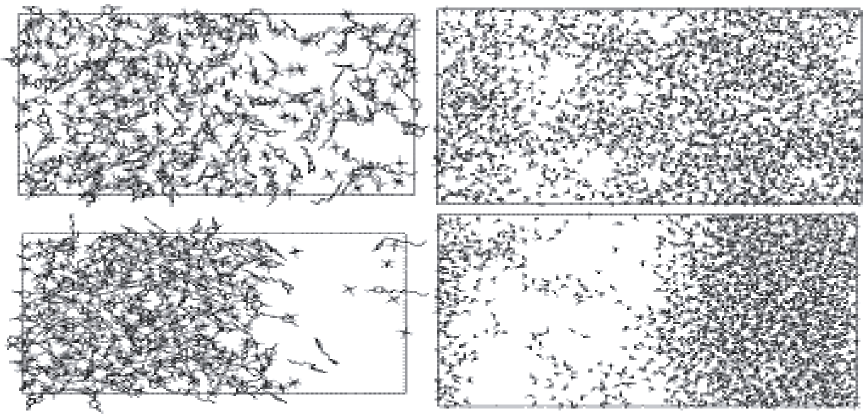

Figure. Aqueous interface with the [BMI][PF_6] (top) [OMI][PF_6] (bottom) ionic liquids. Solvents shown side by side, instead of superposed, for clarity.

Solvent-Solute Interactions of Isomeric Phthalaldehydes in Aqueous Solutions

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As opposed to aliphatic and π-deficient N-heterocyclic aldehydes, which readily in aqueous solutions covalently add water, the majority of benzenoid aldehydes is present in aqueous solutions in less than 3% in the hydrated (geminal diol) form. The only reported exception present some nitrobenzaldehydes. No information has been available on the effect of other electron-withdrawing groups on increased reactivity of the CH=O group towards nucleophilic addition of water. Considerable difference between such reactivity of the three isomeric benzenedicarboxaldehydes is reported.

The 1,3-benzenedicarboxaldehyde (isophthalaldehyde) behaves similarly as the majority of other substituted benzaldehydes and is present in aqueous solutions in equilibrium in less than 3% in the monohydrated form.

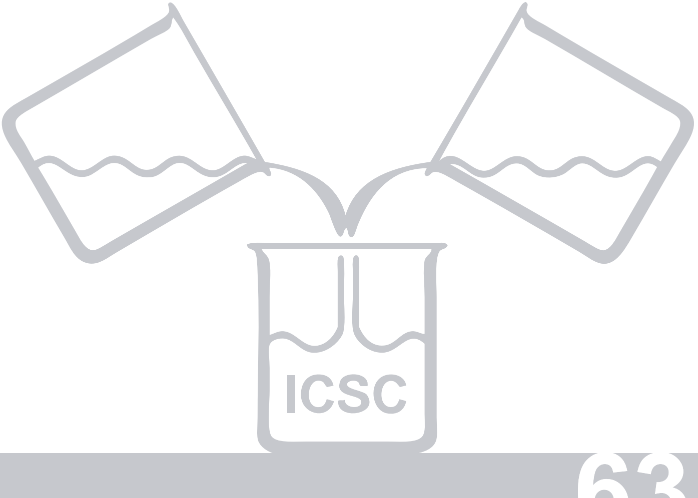
Electrochemical and spectrophotometric evidence proves that the 1,4-benzenedicarboxaldehyde (terephthaladehyde) is present in aqueous solutions in about 15% in a monohydrated form. The effect of the second p-formyl group (as a substituent), even taking into account the probability factor, is larger than the effect of a p-NO_2 group. Larger effect of p-CH=O than predicted by the Hammett $\sigma_{p\text{-}CHO}$ value is attributed to a strong resonance interaction of the two CH=O groups. In unbuffered solutions the rate of addition of water is relatively slow ($\tau_{1/2}$ of the order of 10s).

The 1,2-benzenedicarboxaldehyde (orthophthalaldehyde) is commonly assumed to be present in aqueous solutions solely as a cyclic hemiacetal. Polarographic investigations indicated that in equilibria in aqueous solutions this aldehyde is present in about 10% in unhydrated, in 20% as acyclic monohydrated and in 70% in a cyclic hemiacetal form. These equilibria are established with $\tau_{1/2}$ of the order of 10 min. Understanding of solution chemistry of this aldehyde is of particular importance, as it is widely used as a reagent in determination of aminoacids.

Following analogous additions of aliphatic alcohols was prevented by simultaneous formation of mono- and dihemiacetals and acetals. Qualitatively the reactivity increases in expected sequence: MeOH < EtOH < i-PrOH < t-BuOH.

A.
THERMODYNAMICS, KINETICS AND STRUCTURE

Poster Presentations



Stabilization of Cu(III) with Complexons

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The interest to the Cu(III) complexes is caused by their biochemical role. In different biological systems, the Cu(III) complexes were studied as intermediates in enzymatic and non-enzymatic reactions.[1,2]

We have studied complex formation of Cu(III) with complexons representing polyaminopolycarboxylic and polyphosphonic acids containing fragments of nucleic and essential amino acids. This work allows discussing complexation in terms of biochemical processes involving various ions.

The Cu(III) complexes were prepared from potassium ditelluratocuprate(III) in an aqueous solution.[3] In the presence of complexons, the band at 413 nm in the electronic absorption spectrum, which is characteristic of potassium ditelluratocuprate(III), disappears. This indicates substitution of tellurate ions in the coordination sphere of the Cu(III) ion and formation of more stable complexes without absorption in the visible spectrum.

Investigation of such complexes in the visible spectrum is possible using metal indicators. Foe this purpose, we used murexide (H_5L) and xylenol orange (H_6Z). With the use of the completing ion method, constants of stability for Cu(III) monokis-, bis-, and tris-complexes with murexide were calculated; $\log\beta = 15.53$, 20.01, and 21.17, respectively. High stability of the Cu(III) murexide complexes prevented from use of this indicator for studying competing equilibria in Cu(III) complexation with the complexons.

The electronic absorption spectrum of the Cu(III) complex with xylenol orange contains two bands at 440 and 590 nm and differs from the spectrum of xylenol orange containing only one band ant 440 nm. The constants of stability for the Cu(III) complexes with H_6Z (with the 1 : 1 and 1 : 2 ratios) calculates by the competing ion method were 5.57 and 10.54. Low stability of the Cu(III) complexes with xylenol orange allowed to use this metal-indicator system for studying copper(III) complexonate formation.

The investigation of the system allowed to describe formation of the Cu(III) complexonates with the following schemes:

$CuH_2Z^- + HX^{3-} \rightarrow CuX^- + H_3Z^{3-}$;
$CuH_2Z^- + H_2X^{2-} \rightarrow CuHX + H_3Z^{3-}$;
$CuH_2Z^- + 2H_3Y^{2-} \rightarrow Cu(H_2Y)_2^{3-} + H_4Z^{2-}$.

The values of $\log\beta$ for the Cu(III) deprotonated etylenediaminetetraacetate and bisoxyethylenediuphosphonate complexes calculated by different methods were 16.73 and 17.35, 16.99 and 17.34, 17.64 and 18.51.

The Cu(III) oxyethylenediphosphonates are more stable than the ethylenediaminetetraacetates in terms of both thermodynamics and kinetics. This is in agreement of increase of hardness on the Cu(III) ion.

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Rayleigh-Brillouin Scattering of Aqueous Binary Mixtures

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The Rayleigh-Brillouin scattering measurement has been carried out to the aqueous binary mixtures, such as water-alcohol, water-1,4-dioxane, and water-acetone. The concentration fluctuation contributes to both the Rayleigh intensity and Brillouin lineshape.Rayleigh-Brillouin spectra were obtained using a high-resolution double grating spectrometer (DMDP2000, SOPRA). The exciting light source was an Nd:YAG Laser (DPSS, COHERENT) operating at 532 nm with power of 200 mW. Right angle scattering geometry was adopted with the (VV) configuration. The slit width was adjusted to 30 µm, which correspond to 0.038 cm^{-1} resolution. All spectra were recorded in the frequency range from -0.5 cm^{-1} to 0.5 cm^{-1} at intervals of 0.008 cm^{-1} at room temperature(298 K).A flow cell was used to compare the spectral intensities.

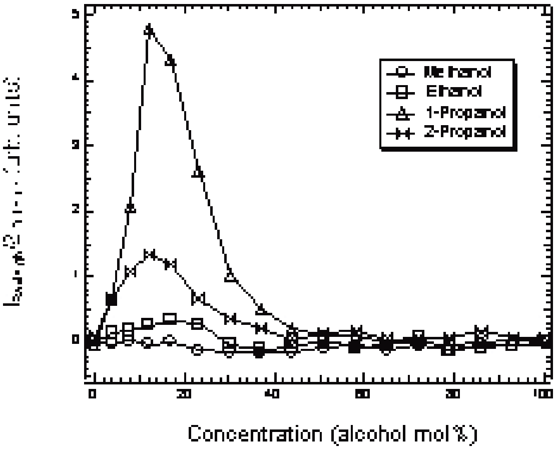

Fig.2 The Landau-Placzek Ratio of water- water mixture

Fig. 1 shows the Rayleigh-Brillouin spectra of water-ethanol mixture. Concentrations are shown in ethanol mole %. The Landau-Placzek ratio is defined by Jexp = $I_{Rayleigh}/2I_{Brillouin}$, $I_{Rayleigh}$ and $I_{Brillouin}$ are integrated intensity of the Rayleigh and Brillouin components, respectively. The Landau-Placzek ratio will depend on the isothermal compressibility, on the Mountain mode, and the microscopic concentration fluctuation of the relevant molecules. Fig. 2 shows the concentration dependence of the Landau-Placzek ratio of water-alcohol mixtures. Isothermal compressibility is subtracted. The maximum of the Landau-Placzek ratio is at 12 mol % and does not depend on the length of the alkyl chain. In other binary systems, water-acetone and water-dioxane, there is a maximum point of the Landau-Placzek ratio in water rich region. It is remarkable that the Landau-Placzek ratio of methanol aqueous solution increase monotonically with increasing concentration. These results mean that the concentration fluctuation in the aqueous binary systems are mainly determined by the properties of water.

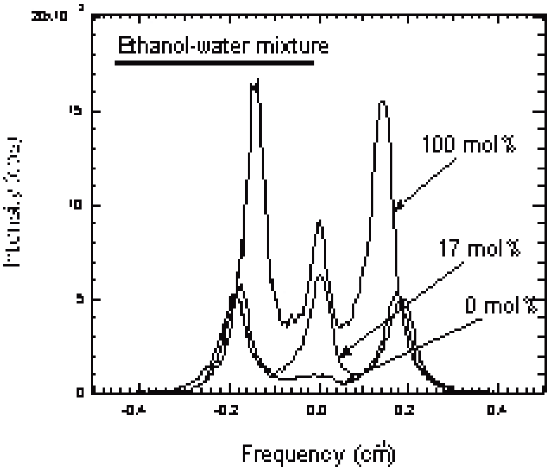

Fig.1 Rayleigh-Brillouin Spectra of ethanol-alcohol binary mictures

Solubilities of Ternary Aqueous Solutions of Fluoro-Hydrocarbons in Alcohols at Temperature 298.15 K and Pressure 101 kPa

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Chemical industries have strong interest in solubilities of organics in water and water in organics. Thermodynamic studies of aqueous-hydrocarbon systems are necessary for the design of liquid-liquid extractors and the design of distillation units.

Solubilities of solutions containing (fluorobenzene+water) and (trifluorotoluene+water) in methanol, ethanol, and 2-propanol were measured in thermostated cell at temperature (298.15 ± 0.01)K and atmospheric pressure. The titration method was used to construct the binodal curves. The ternary liquid equilibrium diagrams are presented for the systems.

The compositions of the mutual phases of both systems were obtained from physico-chemical properties.

The tie-line data were correlated by the UNIQUAC model in addition to the Othmer-Tobias and Hand correlation equations.

The binodal curves and tie-line data were in good agreements. The distribution coefficient data were correlated and the distribution coefficient at infinite dilution for a given solute-solvent pair was obtained. The effect of polarities of the system components on distribution coefficients is discussed.

Synthesis and Thermodynamic Studies of Some α-Naphthyl Amine Derivatives in DMF and THF Solution at 313.15 K

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Some new derivatives of α-naphthyl amine have been synthesized and characterized by TLC, IR, NMR and Mass spectra. Densities, Viscosities and Ultrasonic velocities of these compounds have been measured over the wide composition range at 313.15 K in Dimethyl formamide (DMF) and Tetrahydrofuran (THF). From these experimental data, various acoustical and thermodynamic parameters were evaluated. Some of these parameters are Isentropic compressibility(κ_s), Intermolecular free length(L_f), Solvation number(Sn), Relaxation strength(r), Internal pressure(J_L), Free volume(V_f), Rao's molar constant(R_m), Vander waals constant(b), Molar compressibility(W) etc. The types of interactions in solutions of these compounds in DMF and THF are explained from the evaluated parameters.

Application of the New Developed Solvation Theory to Reproduce the Enthalpies Transfer of Tetraethyl Urea from Water to Aqueous Ethanol, 1-Propanol and Acetonitrile

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The enthalpies of transfer, ΔH_t^θ, of urea from water to aqueous ethanol, EtOH, 1-propanol, PrOH, and acetonitrile, MeCN, are reported. These data are considered in terms of the new solvation theory including variable $(\alpha n + \beta N)$, the net effect of the solute on the solvent-solvent bonding, is positive if there is a net breaking or weakening of solvent-solvent bonds.

Analysis of the data in the mixed solvent systems shows that the solvation of urea is random in all considered solvent mixtures. Tetraethyurea has weaker interaction with water than with EtOH or PrOH in aqueous EtOH or PrOH.

$$\Delta H_t^\theta = x_B \overset{A\to B}{\Delta} H_t^\theta - (\alpha n + \beta N)_A^\theta \left[x'_A L_A + x'_B L_B\right] - x'_B \left[(\alpha n + \beta N)_B^\theta - (\alpha n + \beta N)_A^\theta\right]\left[x'_A L_A + x'_B L_B\right] \quad (1)$$

Where $(\alpha n + \beta N)_A^\theta$ and $(\alpha n + \beta N)_B^\theta$ are the net effect of the solute on solvent-solvent bonds in water-rich region and alcohol-rich region respectively. The enthalpy of transfer from pure solvent A to pure solvent B, $\overset{A\to B}{\Delta} H_t^\theta$, in equation 8 is as follow:

$$\overset{A\to B}{\Delta} H_t^\theta = \Delta H_{12} + (\alpha n + \beta N)_B^\theta \Delta H_B^{0*} - (\alpha n + \beta N)_A^\theta \Delta H_A^{0*} \quad (9)$$

Where $\Delta\Delta H_{12}^\theta$ is the relative strengths of solute-solvent bonds in the pure solvents including intramolecular contribution and if it is positive the solute has weaker interaction with solvent B and the negative value of this parameter indicates stronger interaction of the solute with solvent B. ΔH_A^{0*} and ΔH_B^{0*} are the enthalpies of condensation for pure solvent A and B respectively. L_A and L_B are the relative partial molar enthalpies of solvent A and B respectively.[1-4]

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Spectroscopic Study of the Solvation of Urea in Protic+Aprotic Mixed Solvent

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The infrared spectra of urea have been measured in mixtures of dimethylsulfoxide or acetonitrile with water or methanol. The C=O band of urea shows three distinct absorbances, which are attributed to non-, mono- and di-hydrogen bonded urea. The relative population of the different hydrogen bonded species were determined from analyses of the C=O band shapes. It is found that the variation in the populations of the different hydrogen bonded species can be reproduced by the following equations:

$$mono- = \frac{\frac{K_1}{[H]} + K_3\frac{[S]}{[H]}}{1 + \frac{K_1}{[H]} + K_1K_2\frac{[S]}{[H]^2} + K_3\frac{[S]}{[H]} + K_3K_4\frac{[S]^2}{[H]^2}} \qquad (1)$$

$$di- = \frac{1}{1 + \frac{K_1}{[H]} + K_1K_2\frac{[S]}{[H]^2} + K_3\frac{[S]}{[H]} + K_3K_4\frac{[S]^2}{[H]^2}} \qquad (2)$$

Where $K_2=0.5K^*$ and $K_3=2K^*$. Therefore the experimental data are reproduced using only one adjustable parameter, K*. In all cases the value of K_1 can be determined simply from the proportions of the mono- and di-hydrogen bonded species present in the protic component. The values of K^* provide straightforward information about preferential solvation of the solute chromophore. Thus $K^*<1$ indicates preferential solvation by water or methanol and $K^*>1$ preferential solvation by the aprotic component. Clearly K^* equal to unity represents random solvation.[1-4]

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Limiting Activity Coefficients and Henry’s Law Constants of Organic Aqueous Solutes via Experiment and Molecular Simulation

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The knowledge of the limiting activity coefficient γ_1^∞ and the Henry’s law constant K_H is essential in calculating equilibrium phase concentrations in dilute mixtures and in developing and testing solution theories. Because of their practical importance, these functions are of interest for process engineers, geologists, biologists and environmental chemists. This work deals with the determination of these two interconnected properties for three industrially important systems, aniline(aq), nitrobenzene(aq) and cyclohexylamine(aq), for which the data are rudimentary or missing. To determine the γ_1^∞ and K_H values we employed an experimental approach based on the measurement of the vapour-liquid equilibrium (VLE) and a molecular simulation approach via the Gibbs free energy of hydration ($\Delta_{\mathrm{hyd}}G$).

The experimental part of this work focused on the description of the temperature dependence of γ_1^∞ of the three aqueous solutes. Three VLE measurement techniques, viz. the Rayleigh distillation, headspace analysis and the circulation still method, were used for determination of γ_1^∞ in the temperature range from 298 to 373 K. In order to extend this range towards subambient temperatures and ensure thermodynamic consitency with related thermal properties, information on limiting partial molar excess enthalpies $\bar{H}_1^{E,\infty}$ and heat capacities $\bar{C}_{p,1}^{E,\infty}$ was also employed. As reasonably accurate data on $\bar{H}_1^{E,\infty}$ for the systems studied are available in the literature, only heat capacity measurements were needed. The heat capacities were determined in this work at 298 K using a Picker flow microcalorimeter. Processing simultaneously the data on γ_1^∞ from VLE experiments with the related thermal data allowed us to obtain for the three aqueous solutes truly reliable temperature dependences of their γ_1^∞ in the range from the freezing to the normal boiling point of water.

The simulation part of this work consisted in molecular dynamics simulations in the isothermal-isobaric [NPT] ensemble. A thermodynamically consistent approach to the calculation of the $\Delta_{\mathrm{hyd}}G$ by the finite-difference thermodynamic integration method (FDTI) was elaborated. Aniline in water was chosen as a test system because of the availability of “molecular level” data, such as bond lengths, bond angles, and Lennard-Jones parameters. The simulation package DL_POLY was used to generate a set of 10^5 configurations for 587 molecules of water and 1 molecule of solute (aniline) in a cubic simulation box with periodic boundary conditions. The K_H obtained from the simulated $\Delta_{\mathrm{hyd}}G$ was compared with those from experiments.

Acknowledgement. The support of the Ministry of Education of the Czech Republic (Grant MSM 6046137307) and of the French Government (“these en cotutelle” of M. B.) are acknowledged.

Binding of Dihydrogen Trioxide (HOOOH) on Crown Ether. A Theoretical Study

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There has been considerable progress in understanding of the chemistry of dihydrogen trioxide (HOOOH) during the past 15 years.[1] It is most likely involved in oxidation processes in atmospheric, environmental and biological systems as reactive intermediate. Several compounds such as 1,2-diphenylhydrazine, isopropyl alcohol, cumene and others were found to react with ozone in various organic solvents at low temperatures to form HOOOH.[2-4] Reaction proceeds either over hydrotrioxyl radical $HOOO^{\cdot}$ or hydrotrioxyde anion $HOOO^{-}$. Hydrogen trioxide is relatively unstable at room temperature. The decomposition leads to water and singlet oxygen.[5] Dihydrogen trioxide is, in organic oxygen bases as solvents, far more stable than previously believed, due to relatively strong hydrogen bonds. Basic solvents are able to form 1:1 (H-O-O-O-H·····B) and/or 1:2 (B·····H-O-O-O-H·····B) H-bonded complexes. Half-life of HOOOH in water is just a fraction of a second, while in organic oxygen bases 16 ± 2 min.

Low temperature ozonation of 1,2-diphenylhidrazine included in crown ether in organic solvents produced hydrogen trioxide, crown ether with 1,2-diphenyldiazene (azobenzene) group and other products. HOOOH form relatively strong H-bond with 1,2-diphenyldiazene, thus stabilizing the polyoxide.[3]

Our investigation focused on formation of H-bonded complexes between different size crown ethers and HOOOH with one or two hydrogen bonds. Ab initio calculations at the B3LYP/6-31G(d,p) level of theory have shown 8 to 10 kcal/mol more stable complexes than separated products and relatively small effect of the second H-bond. We also calculated harmonic frequencies and analysed thermodynamic properties.

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Electrical Transport in Aqueous Solutions of Fullerenehexamalonate Electrolytes

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Transport numbers of fullerenehexamalonate macroion constituent in combination with hydrogen, lithium, sodium, cesium and calcium counterions in water solutions have been determined by the indirect moving boundary method at 25ºC. The results show that the transport numbers first increase with augmenting concentration, pass maxima at concentration about 0,01 mol COO^- / l and then decrease. As expected the transport numbers of fullerenehexamalonate macroion constituent diminish from lithium to cesium salt.

From previously measured electrical conductivities[1-3] and transport numbers the fraction of free counterions has been estimated, following the idea of the association of counterions with the macroion.[4] Experimentally obtained values of fractions of free counterions have been compared with those calculated from the solution of Poisson-Boltzmann equation for the spherical cell model.

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Structure of New Heterometallic Ru/Ni, Cu, Zn Complexes with Calix[4]phosphinoxide in Solutions by XAFS Spectroscopy

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Technological processes of extraction and separation of platinum metals from high-level radioactive wastes (HLW) have not developed up to now. An effective extraction of nitro-nitrozo-hydroxo Ru anions by trialkylphosphine oxide (TAPO) to hexane has been revealed recently in a presence of transition metal cations.[1] This phenomenon can be explained by a formation of heterometallic complexes in organic solvent.[2]

Ru*K*, M*K* (M = Ni, Cu or Zn) EXAFS and XANES spectra of 3d- metal complex solutions, and of hybrid (Ru - M^{2+}) systems solutions with calix[4]phosphinoxide (Calix) in toluene and dichloroethane were measured. Local environment parameters of Ru and Ni, Cu or Zn atoms: interatomic distances, coordination numbers, Debye-Waller factors, kinds of environment atoms were determined from EXAFS- spectra analysis. Local symmetry of 3d- atoms environment was determined from XANES spectra. Extraction of nitro-nitrozo-hydroxo Ru anions by Calix to toluene and dichloroethane was studied in the presence of non-ferrous metal cations. Compounds were characterized by IR, NMR and electronic spectroscopy methods.

It was revealed the Ru atom existence at the rigidly fixed distance from the 3d-atoms and decrease of this distance in the order: Cu, Zn, Ni consecutively. This result made evidence of rigid chemical bond between Ru- and M- containing fragments of heterometallic complex. The small increase of the interatomic distance Ru-O (0.03A) in the complex anion under the solution with M^{2+} was detected. Structural parameters of the first coordination sphere of non-ferrous metal cations solvated by the Calix molecules were determined. Structural models have been proposed to heterometallic complexes of several types in toluene and dichloroethane extracts. The obtained data indicate that double or triple coordination of solvated 3d- metals cations to the ruthenium complex could take place *via* oxygen atom of hydroxyl group and NO fragments of nitro-groups linked to the ruthenium atom. This result corresponds to the previous results for solution of hybrid (Ru - M^{2+}) systems with trialkylphosphine oxide (TAPO) in hexane.[2]

Influence of: 1) non-ferrous metal type - Ni, Cu or Zn; 2) ligand type - TAPO, Calix; 3) solvent type - hexane, toluene, dichloroethane, - on the structure of heterometallic complexes was analysed.

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Speed of Sound Measurements Conducted at High Pressures on Aqueous Alcohol and Aqueous Diol Systems at T = 298.15 K

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The pulse echo overlap technique has been used in conjunction with three unique high-pressure cells to measure ultrasonic speeds of sound in dilute aqueous solutions of the alcohols 2-propanol, 2-butanol, 2-propanol, and 2-hexanol and the diols 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol at p = (0.1, 20.0, 40.0, 60.0, 80.0 and 120.0) MPa and T = 298.15 K. A procedure is described by which the sound velocity measurements may be utilised to calculate precise densities and apparent molar volumes. The concentration and pressure dependences of the calculated apparent molar volumes have been modelled using empirical equations which in turn have been used to obtain values for apparent molar volumes at infinite dilution. In addition, measured speeds of sound have been used to calculate isentropic and isothermal compressibilities, and their associated apparent molar properties, for the investigated aqueous alcohol and diol systems. The latter properties have also been modelled as functions of concentration and pressure using empirical equations to obtain the pressure dependences of the apparent molar properties at infinite dilution.

A group additivity approach has been used to model the pressure dependences of apparent molar volumes at infinite dilution. This analysis has provided estimates of the pressure dependences of the contributions of methylene and hydroxyl groups to apparent molar volumes at infinite dilution.

Structural Studies of Aqueous Rubidium Bromide Solutions

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Aqueous rubidium bromide (RbBr) solutions have been studied by neutron (ND) and X-ray (XRD) diffraction, at room temperature and atmospheric pressure. Samples at concentrations of 0.2, 2 and 5 molal were investigated by ND, whereas for XRD, only samples at the two higher concentrations were used. As a reference material, pure D_2O (which was the solvent in each case) was also looked at. The ND measurements were carried out on the PSD two-axis diffractometer at the Budapest Research Reactor, whereas for the XRD experiments, the BW5 synchrotron-based diffractometer, installed at the Hasylab (DESY, Hamburg, Germany), was used. Basic data analyses, which provided (neutron- and X-ray weighted) total structure factors (tsf), were carried out on the raw data from both types of experiment.

The corrected experimental data have been considered as experimental input for Reverse Monte Carlo (RMC) modelling.[1] Partial pair correlation functions, numbers of first neighbours and angular distributions characteristic to local symmetries have been calculated from the particle configurations resulting from RMC. Results from the modelling suggest that in aqueous RbBr solutions the hydration shells of the ions are much less well defined than those in solutions containing smaller ions such as Li^+ and Cl^-.[2]

Classical Molecular Dynamics (MD) simulations have been carried out for five concentrations of the electrolyte. Conditions, particularly interatomic potentials, of the MD simulation were taken from an earlier MD study of the material.[3] Comparison with experimental data was made at the total structure factor level (which is not a common practice yet). Neutron weighted total structure factors calculated from MD were in fairly good agreement with experimental data, especially as far as the (upward) shift of the main (first) peak of the ND tsf is concerned. This suggest that the current MD parameter set is capable of describing changes in the ’water-substructure’, at least qualitatively, as the salt concentration increases. X-ray weighted tsf’s, on the other hand, could not be reproduced so successfully by MD, which means that further refinement of the ion-water (and ion-ion) pair potentials is necessary.

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Ion-Pair Formation of 2,2-Electrolytes from Electric Conductivity Measurements: $MgSO_4$ in Water/1,4-Dioxane Mixtures

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Investigations on the temperature and concentration dependence of electric conductivity of electrolytes belong to the most precise methods yielding information on ion-ion and ion-solvent interaction. Whereas systematic studies of 1,1-electrolytes in many solvents have been reported[1-3] the investigation of 2,2- electrolytes were limited to the water solutions mainly.[4-5]

In this work electric conductivities of diluted solutions of magnesium sulphate solutions in water/1,4-dioxane mixtures at temperatures 5 to 35° C are carried out to exemplify the influence of dielectric constant on the ion pairing of 2,2-electrolyte. The measurements on solution conductivity were carried out on highly pure products and in an inert atmosphere with an equipment yield precise data.

The Fuoss-Justice equation for associated electrolytes based on the low concentration chemical model[6] of electrolyte solutions is applied to yield the limiting conductivities and association constants. From the temperature-dependent Gibbs energy of ion-pair formation the entropy and enthalpy of the association process are available.

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An Ab Initio Study of Hydration Structure of Chain-Like Molecules with Hydrophobic and Side Hydrophilic Groups

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Studies of the hydration structure of complex molecules, which contain hydrophilic and hydrophobic groups are of great interest, because they can point out on the origin of conformation of chain-like molecules in solvents. Theoretical models based on kinetic empirical equations can just to some extent qualitatively reflect processes, which take place in the system chainlike molecule-solvent. In order to get more detailed understanding of hydration processes one has to consider models on atomic level, and even with charge redistribution if possible, because the geometry of molecules is defined by the covalent bonds. The aim of this study was to explore by the ab initio molecular dynamics approach changes in the geometry of chain-like molecules, which contain hydrophobic and side hydrophilic groups, during the hydration process.

We have performed a electron density functional study of equilibrium geometry of molecules CH_3-CH_2-CHOH-CH_2-CH_3 and CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3. The calculations on the second type of molecule were needed in order to understand the tendency in geometry of the chain-like molecule with increasing the number of [CH_2-CHOH] groups. All the calculations were performed in frames of ab initio density functional approach with the Vanderbilt type of pseudopotentials providing cutoff energy of 25 Ry, and the gradient corrected functional in Perdew-Burke-Ernzerhof formulation. The interatomic distances and molecular angles for the molecule CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3 were obtained in good agreement with Jorgensen‘s parameters used for organic molecules.

The geometry minimization procedure for hydrated by thirty two water molecules CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3 at the temperature 293 K was performed within the framework of electronic density functional approach. A description was provided for electronic subsystem of 156 double-occupied electronic states, which form distribution of electronic density between atoms. Optimization of hydration structure permitted both redistribution of electronic density in molecules CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3 and H_2O, and displacements of ions towards local energy minima. As a result of hydration the geometry of the molecule CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3 was changed. In contrast to non-hydrated molecule both OH groups of the molecule CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3 are not parallel anymore, there exists an angle of approximately 60 deg between them. Both OH groups have the length ROH = 0.98 +/- 0.01 Å. The water molecules in hydration structure are on average at the distance 3.5 Å from the charged groups of the molecule CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3, only at the hydrophilic groups OH two water molecules get closer by their oxygens at the distance approximately 2.9 Å to the nearest hydrogens of the hydrophilic groups. Thus, the calculations of hydration structure of the molecule CH_3-[CH_2-CHOH]$_2$-CH_2-CH_3 by the ab initio molecular dynamics point out on the probable changes in orientation of the hydrophilic groups OH due to interaction with the water molecules.

Density and Viscosity Studies of Binary Mixtures of (Aniline + Benzene) and Ternary Mixtures of (Aniline + Benzene + N, N- Dimethylformamide) at (298.15, 303.15, 308.15, and 313.15) K

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Densities and viscosities of binary mixtures of aniline with benzene have been measured over the entire range of composition, at atmospheric pressure, and at (298.15, 303.15, 308.15, and 313.15) K. Excess molar volumes and deviations in viscosity have been calculated from the experimental data. Negative excess molar volume and negative deviations in viscosity values for aniline + benzene systems are due to the interstitial accommodation of benzene molecules into aggregates of aniline. Excess molar volume and deviations in viscosity have been fit to the Redlich-Kister polynomial equation. Further more, densities and viscosities of ternary mixtures of aniline + benzene + N, N-Dimethylformamide have been measured at atmospheric pressure, and at (298.15, 303.15, 308.15, and 313.15) K. From these data, excess molar volumes and viscosity deviations have been calculated. McAllister's three-body interaction model has been used to correlate the kinematic viscosities of binary and ternary liquid mixtures with mole fractions. Several empirical equations have been used to predict the excess molar volumes and viscosity deviations of ternary mixtures.

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Effe*c*t of D and ^{18}O Isotope Substitution on the Absorption Spectra of Aqueous Copper Sulfate Solutions

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The influence of deuterium substitution on the color of hydrated salts was first reported by Bell in 1936 on the solutions obtained by dissolving anhydrous copper sulfate in heavy water and ordinary water: heavy water solution was found to be slightly greener.[1] This difference in tint can also be readily seen between the solid salts $CuSO_4 \cdot 5D_2O$ and $CuSO_4 \cdot 5H_2O$.

In the Mössbauer spectra of the frozen solutions of $FeSO_4 \cdot 7H_2O$ in $H_2{}^{16}O$ and $D_2{}^{16}O$ a significant difference in the quadrupole splitting was observed[2] which further increased in $H_2{}^{18}O$ solution containing 70 mol % $H_2{}^{18}O$. These rather surprising isotope effects (the magnitude of the isotope effect on quadrupole splitting is larger for ^{18}O than for D substitution) were interpreted in terms of the displacement of the water molecules surrounding the ions due to isotope substitution.[3] It can be expected that the displacement of the water molecules surrounding the metal ion might also play a role in the isotope effect on absorption spectra. In this paper the results of the measurements of the absorption spectra of anhydrous copper sulfate dissolved in $H_2{}^{16}O$, $D_2{}^{16}O$ and $H_2{}^{18}O$ in the wavelength range 400 - 1100 nm will be reported.

The absorption spectra of 0.5 aquamolality solutions of copper sulfate in $H_2{}^{16}O$, $D_2{}^{16}O$ and $H_2{}^{18}O$ were determined at room temperature;. both deuterium and ^{18}O isotope substitutions resulted in a decrease of 5 and 1%, respectively, in the integrated absorption coefficient. No shift in the maximum of the absorption band was observed; the absorption band became narrower. The tints of the $D_2{}^{16}O$ and $H_2{}^{18}O$ solutions appear to the human to be very similar and the solutions are slightly greener than the $H_2{}^{16}O$ solution.

The experimental findings that both D and ^{18}O substitutions give rise to the narrowing of the absorption bands and that the visually observed tint of $CuSO_4$ - $H_2{}^{18}O$ solution seems to be much closer to that of $CuSO_4$ - $D_2{}^{16}O$ than to that of $CuSO_4$ - $H_2{}^{16}O$ solution suggest that the amplitudes of the hindered translations of water molecules play an important role in the isotope effect on the absorption spectra of aqueous copper sulfate solution. It is concluded that the observed isotope effects may mainly be ascribed to the change in the closest approach of the first coordination sphere water molecules to the Cu^{2+} ion brought about by isotope substitution.

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Equlibrium Properties of Isotactic Poly(methacrylic Acid) in Water: Osmotic Coefficient and Apparent Molar Volume Measurements

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Marked differences have been found in solution properties of poly(methacrylic acid), PMA, in dependence on its stereoregular structure.[1,2] They suggest that the isotactic form of the acid, i-PMA, behaves as a weaker acid in aqueous solutions in comparison with its syndiotactic, s-PMA, and atactic, a-PMA, counterparts and has a more rigid and stiffer conformation. In this contribution we report the results of osmotic coefficient and apparent molar volume measurements of i-PMA in dependence on the degree of neutralization, α_N, of the polymer.

Isotactic PMA was prepared by the hydrolysis of isotactic poly(methylmethacrylate), i-PMMA. The sample was purified by exhaustive dialysis against water and dried by lyophilization. The tacticity of i-PMMA sample was determined by ^{1}H NMR measurements in deuterated chloroform: it contains 92% of isotactic, 4% of syndiotactic, and 4% of heterotactic triads. The polymer was in the first place characterized by potentiometric titrations and by the determination of its solubility in water. The sample of i-PMA used in this study is not soluble in water below a critical degree of neutralization, α_{crit}, equal to approximately 0.2. The potentiometric titration curves for the acid and alkaline titration of i-PMA are irreversible and display a well-pronounced hysteresis loop. The area of this loop was used to obtain the Gibbs free energy change due to all irreversible changes during the titration cycle.[3]

Osmotic coefficients, ϕ, and apparent molar volumes were determined in dependence on the concentration of the polymer at several fixed α_N values ranging from 0.1 to 1. The α_N values below α_{crit} were obtained by first neutralizing the sample up to $\alpha_N \approx 0.3$ with NaOH, followed by the addition of HCl so that α_N was reduced to 0.1. The excess simple electrolyte that resulted from such procedure was removed by dialysis against water. In this way, thermodynamically meta-stable solutions of i-PMA at $\alpha_N \approx 0.1$ were obtained in which the polymer did not precipitate. The measured osmotic coefficients of i-PMA exhibit a normal behaviour: they are only weakly independent on concentration and increase with decreasing α_N from around 0.25 at $\alpha_N = 1$ to around 0.7 at $\alpha_N = 0.1$. These low ϕ values indicate large deviations form ideality that are caused by strong interactions in such systems. The experimental values were compared with the theoretical ones obtained by using the classical Poisson-Boltzmann equation for the cylindrical cell model. A moderately good agreement was obtained.

The apparent molar volumes, Φ_v, were calculated form the measured densities of solutions and increase with decreasing neutralization in the region of α_N between 1 and 0.4, whereas for α_N below 0.4 they are roughly constant. Φ_v values for i-PMA are lower than the ones for a-PMA in the whole region of α_N. This may be a consequence of a difference in backbone rigidity of chains with different stereoregularity.

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Multinuclear NMR Study of the Structure and Dynamics/Fluxionality of M^{III}-ethylenediamine-tetraacetate ($M(edta)^-$, M = Al, Ga, In and Tl) Complexes in Solution

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Interest in the chemistry of this classical ligand (edta) has been renewed, because of the environmental problem caused by leaking edta containing, radioactive waste water tanks.[1] The transport of metal complexes in the environment, i.e. the interaction of these species with the components of soil by surface complexation could be related to the hydration and the fluxionality of the dissolved complexes. High resolution NMR spectroscopy is superior to study the symmetry of complexes in solution,[2] but there is an obvious need to take into account the intra molecular isomerisation/ fluxionality of the complexes, because a fast rearrangement of the donor atoms (including the water) in the inner sphere might virtually increase the symmetry.

The aim of this paper is to reinvestigate the M(edta)– systems (M = Al, Ga, In and Tl) in solution by ^1H, ^{13}C and ^{27}Al / ^{205}Tl NMR varying the temperature, pH or using different solvents to change the rate of the fluxionality. X-ray structure of the newly prepared mixed valenced thallium-edta, $Tl^ITl^{III}(edta)\cdot 2H_2O$ has also been solved.

The solution structure of the complexes – according to the NMR spectra, see Figure 1– seems to be similar to the structure in solid determined by single crystal X-ray diffraction. Hexadentate edta ligands octahedrally coordinate the central ions in the Al- and Ga-complex, whilst the seven coordinated In^{3+} and Tl^{3+} are hemispherically surrounded by the hexadentate edta and one water molecule is also coordinated in the inner sphere. Temperature dependent ^1H and ^{13}C spectra indicate intra molecular exchange between the axial and the equatorial acetate arms of the $Aledta^-$ and $Gaedta^-$, k_{obs}~1 s^{-1} rate constant can be calculated in case of $Aledta^-$. Density function theory (DFT) calculations show that the dissociation of the axial carboxylate groups is thermodynamically favoured against the same process of the equatorial ones, both for the water catalysed and for the proton catalysed rearrangement.

Although the acetate arms are not fully equivalent in case of the In- and Tl-complexes in solid, the exchange between them in solution are in the ‘fast exchange regime’ both at ^1H and ^{13}C NMR time scale in the 240-320 K temperature range studied in dmso-water mixture.

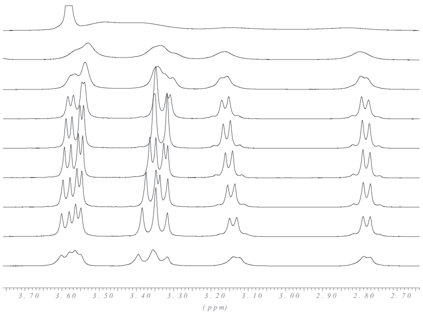

Figure 1. 500 MHz 1H NMR spectra of 0.1 mol/dm3 KAledta in 80% dmso-d6 + 20% D2O. T (K) = 250, 260, 270, 280, 290, 300, 310, 325 and 350 from the bottom to the top, respectively.

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Liquid-Gas Phase Coexistence in Polydisperse Liquid Mixtures. Application of the MSA

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We have shown that a polydisperse mixture of Yukawa hard spheres with factorizable interactions treated within the mean spherical approximation (MSA) and polydisperse mixture of charged hard spheres treated within the MSA and associative MSA belong to the class of truncatable free energy models, i.e. to those systems where the thermodynamic properties can be expressed with a finite set of generalized moments of the distribution function characterizing the system. As a consequence we could map the coexistence relations that are particularly complex for polydisperse systems onto a coupled set of highly non-linear equations for the unknown moments of the daughter distribution functions. Solution of the set of coupled equations for two coexisting phases and for several specific polydisperse mixtures leads us to the phase diagrams in terms of the cloud- and shadow-curves, the critical binodals and binodals for several selected densities of the mother phases. Further we have determined explicitly the daughter distribution functions of the two coexisting phases for several selected pairs of points in the phase diagram and have analysed them in terms of their functional dependence on the mother distribution. The size of the particles of the mother phases is assumed to be distributed according to Beta-distribution and for each particle the ‘charge’ is assumed to be proportional to its surface. Looking at the first two moments of the daughter distribution functions along the shadow-curve and along the binodals we could make quantitative conclusions on fractionation effects induced by the phase transition. From this analysis we observe a rather rich variety of phenomena.

Finally we propose a high temperature approximation and an extension of the analytical solution of the MSA for polydisperse Yukawa hard-sphere mixtures with an arbitrary number of Yukawa tails and choosing them in such a way as to micmic a Lennard-Jones potential. We compare our theoretical results with recently published computer simulation results.[1] Our comparison demonstrate good agreement between theory and computer simulation**.**

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Hydration Structure of Carboxylate Ion Studied by Neutron Diffraction with $^{12}C/^{13}C$ Isotopic Substitution Method

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Time-of-Flight (TOF) neutron diffraction measurements have been carried out for aqueous 10 mol% K2*CO3 solutions in D2O. The 12C/13C isotopic substitution technique was applied to the carbon atom of the carboxylate ion in order to determine the hydration structure around CO32-. Neutron diffraction measurements for sample solutions sealed into Ti-Zr null-alloy cells were carried out at 25 °C using the HIT-II total scattering spectrometer installed at the pulsed spallation neutron source (KENS) in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan.

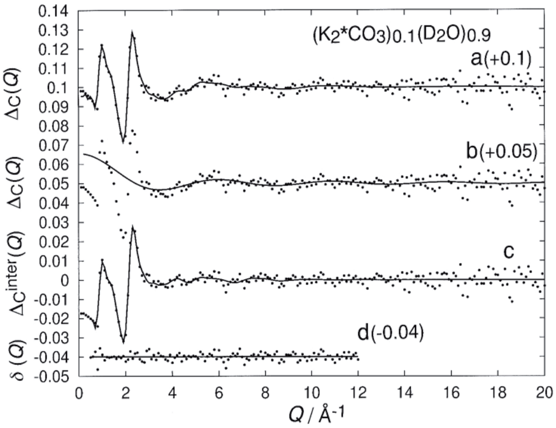

Fig.1. Total (a) and intermolecular (c) difference function, $\Delta_C(Q)$, observed for 10 mol% K2*CO3 solutions in D2O.

The first order difference function1 ΔC(Q) was successfully obtained from the difference in scattering cross sections observed for K212CO3 (98.9% 12C, natural abundance) and K213CO3 (98.8% 13C) solutions (Fig. 1a). The intramolecular C-O contribution was then subtracted from the observed ΔC(Q) (Fig. 1b) to derive the intermolecular difference function, ΔCinter(Q) (fig. 1c), which involves information on the distribution of water molecules around the carboxylate ion. The distribution function, GC(r), around the carbon atom of the carboxylate ion, was obtained by the Fourier transform of the ΔC(Q). A dominant first peak at r = 1.3 Å in the total GC(r) (Fig. 2a) is assigned to the intramolecular C-O interaction. Partially resolved peak at around r = 3 Å appearing in the intermolecular $G_C^{inter}(r)$ (Fig. 2b) indicates the presence of well-defined first hydration shell around the carboxylate ion. The nearest neighbour C...DW (DW: water deuterium) distance, r(C...DW) = 2.68(1) Å, and the coordination number, n(C...DW) = 9.1(5), was determined from the least square fitting analysis of the observed $\Delta_C^{inter}(Q)$.

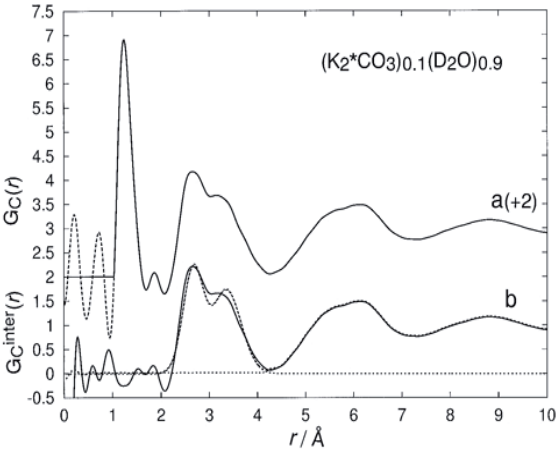

Fig. 2 Total (a) and intermolecular (b) distribution functions, $G_C(r)$ and $G_C^{inter}(r)$, around the carbon atom within the carboxylate ion.

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Photoinitiated Catalytical Aqueous Autoxidation of Sulfur(IV)

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The aqueous autoxidation of sulfur(IV)[1-3] is of considerable current interest in inorganic reaction mechanisms primarily because of its dominant role in acid rain formation. In addition to homogeneous transition metal ion catalysis,[1] photocatalytic pathways can in principle be very important in this system.

In this work, the cerium(III) and iodide ion catalyzed, photoinitiated oxidation of sulfite ion by dissolved oxygen has been studied in strongly acidic aqueous medium. In both cases, a newly introduced technique was used in which a diode-array spectrophotometer is used as a photochemical device.[4] This method can often yield information not usually available from classical photochemical experiments.

The results show that a chain mechanism is operative in both cases and the role of light is only to initiate the chains but not to maintain them. This phenomenon gives rise to relatively high reaction rates and very high quantum yields. The initiation is markedly different in the two systems. In the cerium(III) system, cerium(III) acts as both a photoactive absorbing species and a catalyst for the propagation steps. In the iodide ion system, iodide ion is only a catalyst for the propagation steps and the photoactive absorbing species is presumably the hydrated sulfur dioxide present in the system. Radical chain mechanisms are proposed to interpret the experimental observation in both cases. The most important chain carriers are sulfite, sulfate, and peroxomonosulfate ion radicals. A detailed comparison of the two systems will be presented.

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Influence of Nonionic Surfactant on the Anionic Dye-Cationic Surfactant Interactions

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Interactions between anionic azo dye C.I. Acid Red 88 (AR88) and cationic surfactant cetyltrimethylammonium bromide (CTA) in the solutions of nonionic surfactant Triton X-100 (TX100) in its micellar concentration range were studied at 25 °C by a potentiometric technique using a CTA surfactant cation-selective electrode. The degree of binding of CTA to AR88 in the presence of the TX100 micelles was determined on the basis of the difference in potentiometric curves of the CTA obtained, under the same conditions, in the TX100 solution and in the mixture of TX100 and AR88. According to the theoretical approach to the mononuclear complex formation,[1] the CTA-AR88 complex formation constants, K_1, with and without the presence of TX100 were calculated. The results show that the value of K_1 obtained in TX100 solution is 10^4 times lower compared to the system where TX100 micelles are not present, suggesting that the tendency of CTA-AR88 complex formation as well as the stability of this complex strongly decrease in the TX100 solution. It was also observed that the value of K_1 decreases as the TX100 concentration increases. The results are in perfect compliance with the results obtained with regard to the dodecyltrimethylammonium bromide-AR88-TX100 system.[2] It can be concluded from this that the decrease of K_1 accompanied the CTA-AR88 complex formation in TX100 solution can be attributed to the attractive forces between CTA and TX100, which create a counter-balancing mechanism against CTA-AR88 attractive forces. This is supported by the results of the investigation into CTA-TX100 interactions in the binary mixture, where a high degree of binding of CTA cations to TX100 micelles was obtained.

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The Catalytic Activity of Vanadium Pentoxide on the Electrochemical Oxidation of Hydrogen Sulphide at Glassy Carbon Electrode in Alkaline Solution

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The presence of V_2O_5 species in the bulk alkaline solution is found to promote the oxidation of aqueous H_2S into elemental sulphur. The primary electron transfer and hence the observed anodic current at the glassy carbon electrode is due to the regeneration of V^{5+} species. The reactivity of the present system insignificantly affected by the formation of elemental sulphur since the anodic current dependent upon the diffusion and the amount of V^{4+} species formally produced in the bulk chemical reaction. The electrode process is found to be controlled by mass transport conditions at which the calculated diffusion coefficient of V^{4+} ions was 7.3×10^{-10} m^2/ s. The electrode kinetics under the experimental conditions employing a Tafel – like – plot revealed that the standard rate constant approached a value of 6.6×10^{-5} cm/ s at electrode potentials few millivolts above the open circuit potential. Finally, the sensitivity and the linear range for the detection of aqueous H_2S were achieved in the presence of V_2O_5 species.

Thermodynamic Properties of C_{60} Fullerene Solutions in Pure and Mixed Organic Solvents

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The interactions of fullerenes with organic solvents have become a significant part of fullerene chemistry related to the technological synthesis of this class of compounds.

The aim of this work is to investigate C_{60} fullerene solubility in some pure and mixed organic solvents in wide temperature range; as well to reveal the regularities in solvation changes of the C_{60} fullerene depending on the temperature and mixed solvent composition.

The solubility of C_{60} fullerene in tetrachloromethane – toluene and tetrachloromethane – o-dichlorobenzene mixtures has been studied at the whole solvent composition range and within temperature range of 25–65^{0}C. We have applied the solubility method and differential scanning calorimetry technique to study of C_{60} solubility. The original experimental setup has been utilized for these measurements. According to our preliminary experiments the saturation process requires about 48 hours. The concentrations of dissolved fullerenes have been determined using Liquochrom 2010 chromatograph and chromatograms have been processed with the Multichrom 1.5 program package. The accuracy of our measurements was within 5%.

We found that C_{60} solubility in pure tetrachloromethane is temperature independent in the studied temperature range. In pure toluene and o-dichlorobenzene we observed decrease of C_{60} solubility with increasing of the temperature. We have suggested the equation to account the C_{60} solubility dependence on temperature and composition of mixed solvent. The thermodynamic functions of C_{60} solution process have been calculated using this equation.

It has been reported previously that o-dichlorobenzene, tetrachloromethane and toluene can form the solid solvate complexes with C_{60} fullerene. Our DSC experiments shows that crystallosolvates can be formed both in pure and mixed solvents. The solvate composition depends on the technique used for the preparation of solvates. The possibility of mixed crystallosolvates formation has been also shown in our study. The temperatures and enthalpies of decomposition, as well as composition of solvates have been analyzed.

We have analyzed the experimental data on C_{60} solubility in different organic solvents and derived the correlation equation, which accounts the dependence of thermodynamic parameters of C_{60} solution on dielectric constant, molar volume and refractive index of the solvent. This equation allows us to predict the enthalpy of C_{60} solution at different temperatures.

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Modeling of Excess Molar Volume and Speeds of Sound for Binary Liquid Mixture of Alkoxyalkanols with Alkyl Amines Using PFP Theory and ERAS Model

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The effect of simultaneous presence of ether (-O-) and hydroxyl (-OH) group on thermodynamic properties and corresponding behaviour of alkoxyalkanols in the mixtures is of great important from both practical and fundamental point of view to understand the interaction behaviour. The excess molar volumes of the alkoxyalkanols with substituted amines has been characterized at different temperatures in terms of ERAS model and Prigogine-Flory-Patterson theory which account for the hydrogen bonding effect as well as the free volume effects. The results obtained by adjusting the model parameters reveals a strong cross-association between the unlike molecules in the mixtures resulting from strong negative value for the hydrogen bonding energy and hydrogen bonding volume. The behaviour of ultrasonic speeds and excess molar volumes of the binary mixtures of alkoxyalkanols with n-alkyl amine and substituted amines have been studied. The ultrasonic speeds values have been combined with those of the excess molar volumes converted to densities to give the estimates of the product $K_{S,m}$ of the molar volumes and isentropic compressibility κ_s , and the corresponding excess quantity $K_{S,m}{}^E$. Also, theoretical values of the molar isentropic compressibility $K_{S,m}$ and speed of sound u were calculated using the Prigogine-Flory-Patterson theory with a van der Waal potential energy model. The behaviour of u^D, $K_{S,m}{}^E$ with composition and number of carbon atoms is discussed in terms of interaction.

Thermodynamics of Protonation/Deprotonation of Polyprotic Acids

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Protonation or deprotonation of biologically important polyelectrolytes (proteins, DNA) accompanying helix-coil transitions and protein-protein and protein-DNA binding is crucial for their appropriate function. Moreover, many of the polybasic (polyprotic) acids and their salts are naturally occurring in foods and are essential to normal metabolic processes or are of interest in environmental chemistry. Recently, a general approach to analyze electric conductivities in aqueous solutions of polybasic organic acids is proposed.[1] To better understand the forces that drive protonation/deprotonation of macromolecules the corresponding thermodynamic information ($\Delta G°$, $\Delta H°$, $\Delta S°$, $\Delta C_P°$) is needed. Since natural polyelectrolytes are very complex and contain multiple non-equivalent proton binding sites the detailed thermodynamic analysis of the corresponding titration curves (titration with base or acid) is very difficult.

Therefore, we would first like to describe the protonation/deprotonation in a simpler model system (benzene hexacarboxylic (mellitic) acid). Potentiometric and calorimetric titrations[2] of mellitic acid with NaOH were performed at various temperatures. For the thermodynamic description of the titration curves the concentration of all ionic species together with the corresponding non-ideality of the solution has to be taken into account. Due to the increase of negative charge density on the polyprotic acid at each titration step the proton binding sites are far from equivalent and independent. Despite this fact we successfully described the binding of each of the six protons of mellitic acid in terms of an equilibrium model and the corresponding $\Delta G°$, $\Delta H°$, $\Delta S°$ and $\Delta C_P°$ values.

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The Kinetics of Maceration of Oil from Tobacco (*Nicotiana tabacum* L.) Seeds

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The maceration kinetics of the oil from tobbaco seed (*Nicotiana tabacum L.)* of Preševska Otlja type, collected in the sourordings of Surdulica, South Serbia in 2001 seed was sudied. After harvesting, the seeds were dried, packed in paper bags, stored in a dry, dark place at room temperature and milled before use. n-hexane and petrol ether were used as a solvent. The extraction was carried out at room temperature, 40°C and at boiling temperature, with the plant material-to-solvent ratio of 1:3, 1:5 and 1:10 w/v, for 2,5; 5; 10; 20; 40 and for 60 minutes. The extraction was found to occur in two main stages: The first, washing or the dissolution of oil near the particle surface and the second, diffusion of the oil components from the pores of the plant into the bulk of the extract., The concept of unsteady diffusion through the plant material and the empirical equation of Ponomaryov were used for modelling the kinetics of extraction. The type of solvent, the solvimodul, the plant material-to-solvent ratio and the operating temperature were found to affect the extraction rate and the yield of oil. The maximal yield of tobbaco seed oil (22,3 g oil per 100 g ground seeds) was obtained using n-hexane and at the plant material-to-solvent ratio of 1:10 w/v at boiling temperature in 60 minutes.

Structure, Thermodynamics and Salting-Out of Aqueous Tertiary Butanol Solutions Studied by Atomistic Computer Simulations

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The structure and thermodynamics of aqueous solutions of alcohols is particularly interesting due to the complex interplay of hydrophobic and hydrophilic interactions. Atomistic computer simulations often lack the ability to realistically describe the nonideality of such systems and, in particular, to reproduce properties such as the solution component activities (chemical potentials) and enthalpies and entropies of mixing, which are sensitive to variations of the microscopic liquid structure. The main reason is that most condensed phase force fields are developed to describe the properties of a single-component phase only, and, in cases where binary mixtures are studied, simply two such force fields are combined. We have used the Kirkwood-Buff theory of solution to develop a new force field that correctly reproduces solution component activities as well as the solutions structures of the tert-butanol/water mixture over the full composition range at ambient conditions.[1] We discuss the structural and thermodynamic properties of this mixture as well as the salting-out mechanism of tert-butanol induced by added sodium chloride.

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The Hydrophobic Hydration in Aqueous Solutions of Allyl-Substituted Ammonium Salts

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The aqueous solutions of allyl-substituted and alkyl-substituted ammonium salts have much in common. While the hydrophobic hydration of the tetraalkylammonium salts is investigated in detail now, any information on hydration of allyl-substituted ammonium salts are absent in the literature. In the same time these salts have feature caused by presence by nonsaturated double bonds and by the greater polarity of radical. It can result in differences in hydration of allyl- and alkyl-substituted ions. We carried out studies of ion hydration and mobility of water molecules in aqueous solutions of diallylammonium triflouracetate, diallylmethylammonium trifluoracetate and diallyldimethylammonium chloride. The method of microwave dielectric spectroscopy was used for these purposes, because it allows to find the parameters of dielectric relaxation, and also values of static dielectric permittivity (es). Complex dielectric permittivity was measured by a method of thin dielectric rod in the wave-guide at temperatures 288, 298, 308 K, at frequencies 12.17, 13, 16, 18.9, 22 and 25 HGz (in the region of maximum of dispersion of dielectric permittivity of water). The low-frequency specific conductivity of these systems was measured for determination of the ionic losses. The dispersion of the complex dielectric permittivity in the investigated systems was described by the Cole-Cole equation. Thus the only one relaxation process with the most probable relaxation time takes place at all investigated temperatures and concentrations of salts.

The dielectric relaxation time t was calculated. These values are characterized the changes of the water molecules mobility in the hydration shells of ions. The enthalpy $\Delta H_{\varepsilon}^{++}$, free energy $\Delta G_{\varepsilon}^{++}$ and entropy $\Delta S_{\varepsilon}^{++}$ were calculated from the temperature dependences of the dielectric relaxation time. The growth of τ and $\Delta H_{\varepsilon}^{++}$ of diallylammonium trifluoracetate, diallylmethylammonium trifluoracetate, and diallyldimethylammonium chloride solutions indicate on the structure-making influence of ions on the tetrahedral hydrogen bond net of water. The opposite sign of changes of concentration dependences of τ and $\Delta H_{\varepsilon}^{++}$ is observed in electrolyte solutions with typical hydrophilic hydration (KCl, ect.). It allows conclude that allyl-substituted ammonium salts cause the hydrophobic hydration as well as tetra-alkylammonium salts.

Molecular Simulations of Open Electrolyte Solution Systems: The Expanded-Ensemble Osmotic Molecular Dynamics Method

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We present a novel molecular-level simulation technique called the Expanded-Ensemble Osmotic Molecular Dynamics (EEOMD) method, for studying electrolyte solution systems. The EEOMD method performs simulations at fixed number of solvent molecules, pressure, temperature and overall electrolyte chemical potential. The method combines elements of constant pressure-constant temperature molecular dynamics and of expanded-ensemble grand canonical Monte Carlo. The simulated electrolyte solution systems contain, in addition to solvent molecules, full and fractional ions and undissociated electrolyte molecular units. The fractional particles are coupled to the system via a coupling parameter that varies between 0 (no interaction between the fractional particle and the other particles in the system) and 1 (full interaction between the fractional particle and the other particles in the system). The time evolution of the system is governed by the constant pressure-constant temperature equations of motion and it is accompanied by random changes in the coupling parameter. The coupling-parameter changes are accepted with a probability derived from the expanded-ensemble osmotic partition function corresponding to the prescribed electrolyte chemical potential. The coupling-parameter changes mimic insertion/deletion of particles as in a crude grand-canonical Monte Carlo simulation; if the coupling parameter becomes 0 the fractional particles disappear from the system, and as the coupling parameter reaches unity the fractional particles become full particles. The method is demonstrated for a model of NaCl in water at ambient conditions.

Solvation at Keto-Enol and Acid-Base Equlibria and Meyer's Equation

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In 1912-1914 Meyer[1] proposed for equilibrium constants K of keto-enol transitions an empiricalequation

$$K_{ij}=K_{st,j}E_i \,, \qquad (1)$$

which is not explained theoretically up to now. Indexes i and j in (1) refer respectively to keto-enols (ΚE) and solvents, $K_{st,j}$ corresponds to ΚE, arbitrary chosen by Meyer as standard, and ability to enolization E_i depends only on the ΚE nature but does not depend on solvent. Matrix $\|K_{ij}\|$, evidently, characterizes with special properties: all its lines are proportional one to other ($K_{ij}/K_{i'j}=E_i/E_{i'}$) as well as columns ($K_{ij}/K_{ij'}=K_{st,j}/K_{st,j'}$). Besides, after conversion to logarithms it leads to well known, but also empirical Brönsted equation $\lg K_{i2} = \text{const} + \lg K_{i1}$ for any pair of solvents and analogous equation $\lg K_{2j} = \lg E_2 + \lg K_{1j}$ for any pair of KE's. The reverse conclusion is also true: Brönsted equation leads to Meyer's matrix, so matrixes $\|K_{ij}\|$ for many chemical processes particularly acid-base equilibria possess of properties of Meyer's matrix.

In accordance with (1) K_{ij} is equal to product of two multipliers, the first being depending only on reaction medium (solvent), the second – only on ΚE nature. From the other hand standard Gibbs energy of any reaction which proceeds in homogeneous medium (in our case $\Delta G^0_{ij} = -RT\ln K_{ij}$) always and without any assumptions can be represented[2] as

$$\Delta G^0_{ij} = \Delta G^0_i(\text{vac}) + \Delta\Delta G^0_{ij}(\text{sol}), \qquad (2)$$

where the first member corresponds to reaction proceeding in vacuum, and the second represents an usual linear combination (products minus reagents) of standard Gibbs energies of solvation $\Delta G^0_{ij}(\text{sol})$ for all particles taking part in reaction; in general, it depends on KE as well as on solvent. In a case of keto-enol equilibrium equation (2) is equivalent to

$$K_{ij} = K_i(\text{vac})\cdot\exp[\Delta G^0_{ij}(\text{sol, Ketone}) - \Delta G^0_{ij}(\text{sol, Enol})]/RT. \qquad (3)$$

It is well known (see, for example,[2]) that solvation energies for an molecule in a good approximation can be represented as additive sum of its fragments. Therefore, in brackets of equation (3) leaves only the difference S_j between contributions in $\Delta G^0_{ij}(\text{sol})$ due to functional groups of both tautomeric forms, which depends on solvent but for a series of related KE's does not or slightly depend on the nature of a given KE, while contributions in $\Delta G^0_{ij}(\text{sol})$ from all other parts of molecules are canceling. Hence we obtain

$$K_{ij} = K_i(\text{vac})\cdot\exp S_j/RT \qquad (4)$$

as natural basis of Meyer's equation for keto-enol transformation, since $K_{st,j} = K_{st}(\text{vac})\cdot\exp S_j/RT$ and $K_{ij} = K_{st,j}K_i(\text{vac})/K_{st}(\text{vac})$, i.e. E_i in (1) is equal to $K_i(\text{vac})/K_{st}(\text{vac})$. Corresponding elements of any two columns j and j′ now relate one to other as $K_{ij}/K_{ij'} = \exp[S_j - S_{j'}]/RT$, this ratio being independent of i. So, all properties of Meyer's matrix in discussed particular case with KE's result simply from additivity rule for Gibbs energies of molecules' solvation.

In the paper will be discussed matrixes $\|\lg Kij\|$ for keto-enol, acid-base and some other equilibria which obey Meyer's equation, bases of its application in the latter systems, optimisation of matrix parameters (for matrix i x j there is i+j–1 independent parameters) and ways of distinction between series of related and not so tightly related compounds.

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Electrolyte Inclusion in Disordered Material

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Porous systems are used in many applications such as selective catalysis of chemical reactions, separation of compounds, and adsorption and exchange of specific ions. To this end, better understanding of properties of fluids adsorbed in porous materials is important for basic research and technology as well. Theoretically porous materials filled with liquid may be considered as partly-quenched systems,[1-4] i.e. materials in which some of the degrees of freedom are quenched, and others are annealed and allowed to equilibrate. The ensemble average used to calculate the thermodynamic properties in such systems becomes a double ensemble average: first over the annealed degrees of freedom, and then over the all possible values of the quenched variables. In this respect the partly-quenched systems differ from regular mixtures. Partly-quenched electrolyte systems were recently studied by using the replica Ornstein-Zernike (ROZ) integral equation theory in the hypernetted chain (HNC) approximation, and the grand canonical Monte Carlo simulations.[4-8] In the present contribution we are interested in the excess chemical potential of electrolyte absorbed in the material containing i) neutral material containing charges, ii) disordered charged material, iii) dipolar molecules. In the first two examples the matrix is formed from primitive model electrolyte quenched at temperature T_0, while in the last example (iii) the matrix contains quenched dipolar molecules. The dipoles were represented as fused charged hard-spheres and the matrix component is assumed to be formed by a rapid quench from the fluid equilibrated at temperature T_0. It is assumed that the structure of the matrix corresponds to an equilibrium state of the dipolar fluid. The model of adsorbing electrolyte corresponds to +1:–1 size symmetric primitive model electrolyte. In all the cases solvent is represented as dielectric continuum. The temperature, T_1, (and dielectric constant, ε_1) of observation may differ from conditions of matrix formation T_0, ε_0. Numerical results for this system were obtained using the Grand canonical Monte Carlo method. Thermodynamically the situation corresponds to the well known Donnan equilibrium. The results for adsorption isotherm depend strongly on both temperatures and dielectric constants as also on concentrations of all components. It was found that the dipolar fluid adsorbs smaller amount of electrolyte than an equivalent quenched mixture of positive and negative ions. The computer simulation results for structural and thermodynamic properties were obtained for a set of model parameters and concentrations. These calculations were compared with the new results for the matrix formed from uncharged dumbbells and with isotherms were both components were primitive model electrolytes. The comparison will be made with similar calculations of adsorption in pores with well defined geometry.[9]

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Dielectric Relaxation and Structural Changes of Water in Salt Solutions with Hydrophobic and Hydrophilic Hydration

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The general relations between dielectric relaxation and structural effects in aqueous salt solutions are considered. The analysis is carried out on the basic of new structural model and experimental high frequency dielectric data. The model of hydration shells is based on a principle of the complementary organization of the first coordination sphere of ions, intermediate layer and tetrahedral bulk water. The higher (the lower) is this complementary degree (in compare with water) – the more (the less) is the stabilization (the structure-making effect) or destabilization (the structure breaking effect) of water. It can be determined from the geometrical models or from data of crystal clathrate structures. The structural variations of hydration shells should be accompanied by an increase or decrease in the degree of bonding, orientation order and dynamics of water molecules. For time (τ) and enthalpy ($\Delta H_\varepsilon^{++}$) of dielectric relaxation in the first case: $\tau_s > \tau_{H2O}$ and $\Delta H_s^{++} > \Delta H_{H2O}^{++}$ and in the second case: $\tau_s < \tau_{H2O}$ and $\Delta H_s^{++} < \Delta H_{H2O}^{++}$.

The method of the microwave dielectric spectroscopy (7-120 or 7-25 GHz) is used for the investigation of salt solutions in a wide concentration range. The aqueous electrolyte solutions are conductive liquids. The low frequency conductivity was measured at frequency 1 kHz for calculation of ionic losses at the same temperature interval. The values of static constant (ε_s), τ and $\Delta H_\varepsilon^{++}$ were obtained in temperature range 283-313K or 288-308K for 31 binary systems. They include the solutions of fluorides, chlorides, nitrates, sulfates, formates, acetates, propionates of alkali metals and the solutions of tetramethylammonium, tetraethylammonium, tetrabutylammonium chlorides, tetrabutylammonium formates, acetates and propionates. We worked out the classification and determined the properties connected with hydrophobic or hydrophilic hydration of anions and cations. The temperature effects are considered. Non-additivity of changes of relaxation characteristics in row of the systems is a result of the mutual hydration influence of anions and cations. The above-mentioned geometrical model of structural changes of water and the data on hydration interactions of ions allow to explain the difference of dielectric relaxation dependencies for different solutions.

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Establishing Recommended Data on Thermodynamic Properties of Hydration for Selected Organic Solutes - An IUPAC/IAPWS DATA Project

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The objective of the project is to establish a database of thermodynamic properties of hydration (TPH) for approximately 200 selected organic solutes at reference condition of 298.15 K and 0.1 MPa and for a limited number of solutes also as a function of temperature and pressure up to the near-critical region of water. TPH covered in the project are the Gibbs energy of hydration $\Delta_{\mathrm{hyd}}G_{\mathrm{s}}^{\mathrm{o}}$, and its temperature and pressure derivatives (the enthalpy of hydration $\Delta_{\mathrm{hyd}}H_{\mathrm{s}}^{\mathrm{o}}$, the heat capacity of hydration $\Delta_{\mathrm{hyd}}C_{p,\mathrm{s}}^{\mathrm{o}}$ and the partial molar volume at infinite dilution ($V_{\mathrm{s}}^{\mathrm{o}}$), most other TPH result from their combinations. The values of TPH for solutes covering different molecular structures will be calculated from the reliable experimental data for aqueous and pure solutes. The established database will be used as a standard for testing and establishment of new physico-chemical models and methods of molecular simulation as well as for developing semi-theoretical prediction schemes of interest for chemical engineering, power cycle chemistry, environmental chemistry and geochemistry.

This project is carried out under auspices and support of the International Union of Pure and Applied Chemistry (IUPAC)[1] and the Association for the Properties of Water and Steam (IAPWS)[2] in the period between January 2005 and June 2007. The planned outcome will be i) a technical IUPAC report and an IAPWS guideline, ii) a comprehensive article to be published in the Journal of Physical and Chemical Reference Data, iii) a database freely accessible through the IAPWS and IUPAC web pages. The project requires collaboration of researchers having complementary knowledge in data evaluation and in different experimental techniques used for obtaining data for aqueous and pure solutes. The following groups are participating so far (only the name of the principal investigator and the Institution are given): V. Dohnal and coll. (Institute of Chemical Technology, Prague, Czech Rep.), R. Fernandez-Prini and coll. (CNEA, Buenos Aires, Argentina), M. Frenkel and coll. (NIST, Boulder, USA), A.H. Harvey (NIST, Boulder, USA), V. Majer and coll. (Blaise Pascal University / CNRS, Clermont-Ferrand, France), J. Sedlbauer and coll. (University of Liberec, Czech Republic) and A.H. Shock and coll. (Arizona State University, Tempe, USA). An important milestone of the project will be organization of a Workshop during the International Conference on Chemical Thermodynamics 2006 in Boulder.

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MD Study of Temperature Dependence of Water Vibrational Spectrum

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Vibrational spectroscopy studies show that the bulk water bending band becomes narrower with increasing temperature.[1] Since this counterintuitive effect is not associated with the quantum nature of nuclear motion a classical molecular dynamics (MD) simulation is expected to reproduce it already in the classical limit. We have performed a classical MD simulation of flexible Simple Point Charge (SPC) and extended SPC (SPC/E) water models to determine the temperature dependence of the bulk water vibrational spectrum. The intramolecular water potential, proposed by Toukan and Rahman, including a stretch-bend coupling term, was applied. We performed MD simulations at -4 ºC and 80 ºC to compare the calculated vibrational spectra, in particular the band associated with the bending mode, with the experiment. The experimentally determined narrowing of the bending band with increasing temperature is not reproducible by MD simulation with the applied force field. However, the results show that this approach succesfully reproduces all other experimentally observed spectroscopic properties of bulk water.[2]

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Comprehensive Infrared, Raman and Theoretical Studies of Hexa- and Nona-Aqua Complexes of Different Metals

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Metal ions have a great tendency to form complexes with water molecules. The study of structure and bonding of aqua complexes is always a difficult task especially in solution. Infrared and Raman spectroscopy and theory of vibrations with combination of EXAFS (extended X-ray absorption fine structure spectroscopy) and LAXS (large-angle X-ray scattering) can be used for studies of symmetry and bonding properties.

Spectroscopic and theoretical studies of aqua complexes of general composition will be reported for:

1. $[M(OH_2)]^{n+}$ of divalent (M(II) = Al, Ga, In, Tl) and trivalent (M(III) = Al, Ga, In, Tl) metal ions in aqueous solution,[1] other trivalent cations (M(III) = Ti, V, Cr,Fe, Co, Ru and Ir) partly using experimental frequencies for solid or glassy states.
2. Halide and pseudohalide complexes of octahedral structures: $[TlX_n(OH_2)_m]^{(3-n)+}$, X = Cl, Br, CN,[2] $[(NC)_5Pt\text{-}Tl(H_2O)_x]^{n-}$, (X = 1, 2, 3),[3] $[Hg(OH_2)_2(CF_3SO_3)_2]_\infty$, $[Tl(OH_2)_3(CF_3SO)_3]$.[4]
3. Trivalent rare-earth ions of general composition $[Ln(OH_2)_9]$ $(CF_3SO_3)_3$ with tricapped trigonal prismatic coordination (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).[5]

Force field study of aqua complexes has been performed in most cases for the first time. In some cases D_2O complexes have been also studied.

Special attention has been paid to the metal-oxygen vibrational modes. Due to our broad variety of complexes (46 molecules), we were able to obtain a general correlation between bond distances and stretching force constants. Very good correlations have been observed for complexes of homologue series. Other structurally important parameters like coordination numbers and symmetry (point group) of the complexes have been established.

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Molecular Dynamics Simulations with Polarizable Models: Zn(II) Solvated in DMSO

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Properties of solutions of Zinc(II) ion in Dimethyl Sulfoxide (DMSO) were studied by classical simulations with newly developed model potentials and by means of Car-Parrinello molecular dynamics simulations.

For the classical simulations, a 16-parameter model potential of the general form:
$U = U_{electrostatic} + U_{short\text{-}range} + U_{polarization}$
was assumed. The electrostatic interactions were described by the Ewald sum, the short-range potential is of the Buckingham ($\sim r^{-6}$) type and the polarization term is implemented via a shell model.

Interaction energies were computed for several hundred configurations at the MP2/aug-cc-pVDZ (6-311+G* for Zn) level. Then the free parameters were fitted to the ab initio energies as a function of the various (Zn-S, Zn-O, Zn-C, Zn-H) distances.

Systems containing 64 to 256 molecules of DMSO were simulated at room temperature in the NVT ensemble. In all simulations, it was found that Zinc (II) is hexacoordinated by DMSO. The structural properties of the solvation shell and the bulk were analysed in terms of radial and angular distribution functions.

In addition, we used the Car-Parrinello (CP) method – in which solvent polarizability is included a priori - with ultrasoft pseudopotentials to perform molecular dynamics simulations on Zn^{2+}/DMSO clusters of different size. The results of the classical and the CP simulations are compared.

Calculation of the Hydrational Free Energy Difference Between Pyridine and Its Methylated Derivatives by Computer Simulation Methods

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The difference of the hydrational free energy of pyridine and its methyl as well as symmetric dimethyl derivatives has been calculated by the method of free energy perturbation. In order to check the precision of the results obtained we have repeated the calculations using different grids of the paths along which pyridine is transformed to its methyl-substituted derivatives, and also by using thermodynamic integration over various different paths. Besides the hydrational free energy the difference of the energy of hydration of pyridine and the methyl- and dimethylpyridines has also been determined.

The obtained results clearly show that the hydrational free energy of the pyridine derivatives becomes more negative with each additional methyl groups. However, the precision of the calculation does not allow us to draw any conclusion on the dependence of the hydrational free energy on the location of the methyl group. The analysis of the Coulombic and Lennard-Jones contributions to the hydrational free energy differences has shown the dominance of the latter term.

The comparison of the hydrational energy and free energy values has shown that there is a strong compensation effect between the energetic and entropic terms of the free energy: while the hydrational energy of the solute decreases considerably with each additional methyl group (due to the dispersion attraction between the methyl group and the surrounding water molecules), the entropy of the system is found to be decreased by about 30 J/mol K (and hence, at 300 K, the entropic contribution to the free energy to be increased by about 9 kJ/mol) by each methyl group. Due to their opposite signs, the entropic and energetic contributions largely cancel out each other, resulting in about an order of magnitude smaller value of the free energy.

Molecular Dynamics Study of Aqueous Uranyl in Hydrophilic Mesoporous Confinement: The Case of Slit-Like Pore in Amorphous Silica

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Molecular dynamics simulations are used to study structural and dynamic properties of water and aqueous solutions of uranyl ion adsorbed between two walls of amorphous silica. Calculations are performed for the flexible SPC water model in the atomistically detailed pores with sizes in the range of 2.0-5.0 nm. All simulations are carried out in NVT ensemble using Nosé-Hoover thermostat and with two-dimensional periodic boundary conditions applied. The hydroxyl groups bearing on the pore surfaces lead to the wetting phenomena and affect strongly the mobility of water molecules. A few of surface hydroxyl densities are considered. The aqueous solutions of uranyl ion adsorbed in the pores are studied at the room temperature, for different amount of water. A series of radial distribution functions of aqueous solutions and water density profiles are calculated to illustrate a relative arrangement of molecules in the pores. The layered structure of molecules inside the pores is observed. The self-diffusion coefficients of confined water are obtained as well. The effect of hydroxylated silica pores on the formation of uranyl hydrate complexes is discussed within this study. Due to the binding interaction between the uranyl and the surrounding water molecules the hydrate complex with pentagonal bipyramidal symmetry appears in the bulk water. However, the hydrophilic pore surfaces presence causes changes in the uranyl hydrate, particularly on its contact with silica wall, where surface hydroxyl replaces water molecule in the first shell of the complex. The self-diffusion coefficients calculated from mean-square displacement functions indicate that the water mobility increases with a reducing of surface hydroxyl density and decreases when the uranyl ion is present in the simulation box.

Volumetric Properties of Coenzyme Q10 in Supercritical Carbon Diokside

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Accurate data on volumetric properties are required for design, development and construction of supercritical fluid processes. The densities of coenzyme Q10 in supercritical carbon dioxide were measured with vibrating tube densimeter at 35, 40, 50 and 60 °C and in the pressure range from 10 to 40 MPa. The reliability of the technique has been verified in our previous works and in the present work they were checked comparing our experimental densities of pure carbon dioxide with literature data. Partial molar volumes, apparent molar volumes, isothermal compressibilities, isobaric thermal expansivities and internal pressures were calculated from obtained densities.

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Kinetics of G-Quadruplex Folding and Unfolding

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Guanine-rich tracts of nucleic acids can form four-stranded structures under appropriate conditions of high Na^+ or K^+ ionic strength. These structures, G-quadruplexes, adopt a variety of folds, dependent in part on whether they are intra- or intermolecular. All quadruplexes contain the basic repeating motif, the G-quartet, which comprises four guanine bases held in plane by Hoogsteen hydrogen bonding. Typically, three or four G-quartets are stacked one on top of each other within a quadruplex, held together by π - π non-bonded attractive interaction. Guanine-rich sequences that can potentially form quadruplexes, also occur at the ends of chromosomes, which consist of tandem repeats of simple G-rich sequences.[1] To determine the molecularity of such quadruplexes together with the ΔG, ΔH and ΔS of their formation, a combination of several experimental methods has to be used.

NMR studies have shown that in aqueous solutions the $d(G_4T_4G_3)$ and $d(G_4T_4G_4)$ molecules in the presence of some cations form structures that exhibit properties characteristic of bimolecular quadruplexes.[2,3] In an attempt to investigate the conformational behavior of $d(G_4T_4G_3)$ and $d(G_4T_4G_4)$ structures formed in the presence of Na^+ and K^+ ions and to determine the thermodynamics of their formation we have employed a combination of spectroscopic (UV, CD) and calorimetric (DSC) techniques. Our result show that unfolding and folding of the two bimolecular quadruplexes can not be described by equilibrium thermodynamics.. Instead non-equilibrium thermodynamics has to be used. The kinetics of denaturation and formation of bimolecular quadruplexes will be discussed.

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XAFS Study of Ln(III) Aqua-Ions and Ligand Exchange Rate of Water Molecules

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Nowadays it is well established that a thorough understanding of many chemical properties of ionic solutions should be based on a precise knowledge of their coordination geometry. Therefore, the X-ray Absorption Fine Structure (XAFS) method has become an important experimental method for the examination of the local atomic environment of metals in solutions.[1-4] Moreover, the ligand exchange rate constant, k_{ex}, is closely related to the Debye-Waller (DW) factor value obtained by XAFS and anharmonicity of the potential between metal ions and water molecules. Miyanaga et al.[5] suggested a simple correlation between the DW factor (σ^2) and the exchange rate constant for water exchange for Me^{2+} aqua-ions when plotting (R^4/σ^4) against log(k_{ex}). Nevertheless, the previous XAFS results (R^4/σ^4) on Ln^{3+} aqua-ions in solutions are an example of the controversy. Moreover, the interesting question remains: 'What is the second hydration shell contribution in the XAFS'. The problem is usually explained by strong first shell MS contributions competing with the second hydration shell signal.[1] Also in the simplest case, as octahedral aqua ions, controversy exists. Therefore, we have done the interpretation of XAFS of the second hydration shell in the solutions within the multiple scattering formalism and/or hydrogen contribution to answer this point.

New high accuracy measurements at L_3-edges have been done for Ln^{3+} (La, Ce, … Lu) aqua ions to check the ultimate limits of the XAFS cumulant analysis. The remarkable improvement of experimental data quality and analysis procedures has allowed to measure the local Ln-O expansion and asymmetry of Ln-O radial distribution function (third cumulant). For the first time the local structure has been established for the first shell of Ln^{3+} aqua ions with subpicometer accuracy ($3\cdot10^{-3}$ Å). The dynamic properties of the complexes are related to the structure of the first coordination sphere.

A set of peaks, located beyond the first shell and responsible for the high-frequency contribution in the XAFS signal, is attributed to the multiple-scattering effects within the first coordination shell of rare-earth ions. Based on comparison with four different cluster models, one can conclude that the first shell polyhedron around rare-earth ions has dynamically varying shape, which can be considered as distorted bicapped trigonal prism.

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An Ab Initio Investigation of Multiply Charged Anions

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The structure and vibrational frequencies of hydrated perchlorate, sulfate,[1] and phosphate[2] have been investigated by one of the authors. It was noticed that the Hartree-Fock frequencies of the gas-phase ions, and those solvated by water molecules, were in reasonable agreement with experiment, whereas those at the MP2 level were severely underestimated. Was this a result of an inadequate basis set, a deficiency of the correlated treatment, the lack or inadequacy of a hydration model, or some other effect? An attempt will be made to answer this question.

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An Ab Initio Investigation of the Second Hydration Sphere of Metal Cations

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The structure and vibrational frequencies of hydrated metal cations is a subject of longstanding interest by one of the authors,[1-2] who was the first to publish a minimum-energy structure, of symmetry T, of a metal cation with eighteen water molecules, after initial constraints[3] to symmetry T_h were demonstrated to be incorrect.[4] A lower energy structure of symmetry S_6 has been found by another group.[5] A re-examination of various symmetries of the hydrates of Mg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, and In^{3+}, will be presented in an attempt to find the global minimum.

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Intermolecular Nuclear Overhauser Effect in the Investigation of Preferential Solvation Phenomena: Transient 1D NOE Spectroscopy of Carbohydrates and Fatty Acid Derivatives in Binary Solvent Mixtures

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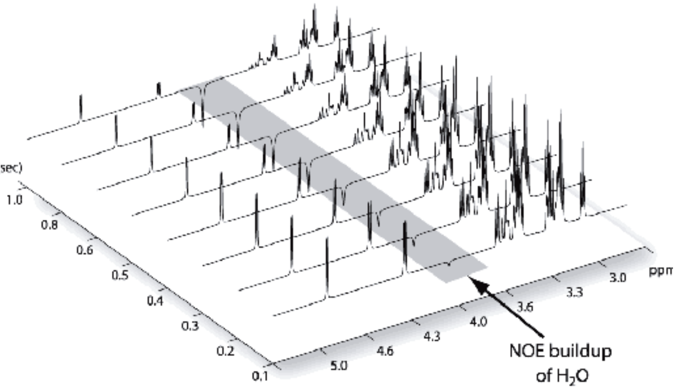
When a substance is dissolved in a mixture of two or more solvents, its solvation shell may have a different composition with respect to the bulk solution: in this case, the solute is said to be *preferentially solvated* by one cosolvent.[1]

In the assortment of available experimental techniques, many recent studies have employed two-dimensional nuclear Overhauser spectroscopy (NOESY) to probe preferential salvation.[1-3] Nonetheless, the use of such a technique is often limited by the low sensitivity which stems from the intrinsic weakness of the observed intermolecular dipolar interactions. One-dimensional NOESY experiments based on double pulsed field gradient spin-echoes (DPFGSE)[4] can partially overcome the aforementioned limitations by delivering high sensitivity at low time costs. Moreover, a properly tuned *solute-to-solvent* magnetization transfer allows for simultaneous observation of signal buildup on multiple solvent resonances, so that only one single experiment is needed to probe the solute solvation shell.

Following this idea, we have set up a pulse sequence tailored to investigate the preferential solvation of carbohydrates in binary aqueous mixtures:[5] as expected, these solutes exhibit a marked preference for water, yet to an extent depending on their hydroxyl topology. The same experimental protocol has been subsequently adapted to investigate the preferential solvation of fatty acids derivatives in binary mixtures of organic solvents. Also, possible site-specific cation-anion interactions in ionic liquids have been searched for by means of the DPFGSE-NOE approach. Advantages and limitations of this technique are discussed in the present communication.



Glucose-to-water NOE buildup

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Thermodynamic Functions of Activation for Viscous Flow of Cyclohexylsulfamic Acid in Aqueous Solution

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Cyclohexylsulfamic acid in the form of its sodium or calcium salts is an intense sweetener. In the process of sweet taste chemoreception the first step requires that the hydrated molecule or ion reaches the region of sweet receptors in the taste epithelium. This process depends on the nature of the solution, i. e. on the volumetric and transport properties, as well as on the structure of the sweeteners. Both are relevant to the kinetic of mouth movement during tasting. Hydration effects in particular are extremely sensitive to the stereochemical details of the solute, which are also affected by the molecular configuration. Furthermore, the structure of water should influence the conformation of a sweetener molecule or ion in solution. Transport parameters of electrolyte solutions such as ionic conductance and viscosity can provide information concerning the nature and kinetic entities from which, for an associated electrolyte, the ion-solvent and the molecule of solute-solvent interactions can be inferred.

With this in mind, the viscosities of aqueous solutions of cyclohexylsulfamic acid were measured up to 0.25 mol kg^{-1} in the temperature range from 293.15 to 323.15 K. The relative viscosities of dilute solutions was represented by the Jones-Dole equation and the values of the coefficient B_i referring to the free ions and of the corresponding coefficient B_d for the undissociated acid were evaluated. The coefficient A was calculated from the conductivity measurements on the basis of theoretical consideration of ion-ion interactions in viscous flow. Applying Eyring's theory of the transition state, the partial free energy, entropy and enthalpy of the ionic and undissociated pars of the acid at infinite dilution were obtained. From the partial molar thermodynamic function of activation for viscous flow and partial molar volumetric data of solute and solvent at infinite dilution, the viscosity coefficients B_i and B_d and their temperature derivatives were calculated and compared with the values of the viscosity coefficient obtained directly from the concentration dependence of the relative viscosities. On the basis of a modified Einstein viscosity law and from a fictious splitting of the process of hydration of the ions and undissociated acid into two consecutive processes, the average hydration numbers of the solute was determined.

Molecular Dynamics Simulation of the Structure of Ion Solvation Shells in N,N-Dimethylformamide

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New interaction potentials for ion - N,N-dimethylformamide (Na^+, K^+, Cl^-, Br^-) based on quantum-chemical calculations were constructed. The ion-DMF interaction energies were determined using the Gaussian-98 program at the level Hartree-Fock approximation with the 6-311G(d,p). The molecular dynamics simulation of the ion – DMF systems was performed for a canonical NPT ensemble. For the Na^+ and K^+ all radial distribution functions that characterized the position of the cations with respect to the three base DMF atoms {$g_{iO}(r)$, $g_{iC}(r)$, $g_{iN}(r)$] had fairly well-defined second maxima in addition to the first high and narrow ones. The first and second maxima were separated by deep minima. So the fluctuations of positions of DMF molecules not only in the first but also in the second solvation shell were very insignificant. All the radial distribution functions for the chloride ion show a weakly defined tendency for the formation of second peaks, which lead us to conclude that the chloride ion has a weak coordination action on solvent molecules outside the first solvation shell. The Br^--DMF radial distribution function, unlike those for the other ions, is characterized by fairly broad and low peaks. The presence of several low peaks is evidence of different solvent molecule orientations with respect to the ion; that is, the first solvation shell has a comparatively disordered structure. For cations studied a temperature increase very insignificantly increased fluctuations of the nearest environment of the ions, and all changes took place in the second solvation shell. The Cl^-–DMF radial distribution shows that the temperature effects on the orientation of solvent molecules in the first solvation shell are substantial. A temperature increase results in the reorientation of one or two DMF molrcules in the first solvation shell: they orient their methyl groups positioned cis to oxygen toward the anion. The different orientations of solvent molecules with respect to the bromide ion are observed at all temperatures.

So analysis of the ion-DMF radial distribution functions shows that the ability of the ions to coordinate solvent molecules decreases in the series $Na^+ > K^+ > Cl^- > Br^-$. The cations have strong coordinating action on solvent molecules up to the third solvation shell, whereas well-defined structure is only observed in the first solvation shell of Cl^- and no predominant orientation of DMF molecular can be identified even in the first solvation shell of Br^-. For the ions with strong coordinating effects (Na^+ and K^+), weak temperature dependence of structure of their solvation shells have been observed. With the chloride ion, the temperature substantially influences the orientation of solvent molecules in the first solvation shell. As the bromide ion has comparatively solvation shell at all temperatures, it does not make sense to consider temperature effects for it.

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Liquid-Liquid Equilibrium in the Ternary System Water + Triethylene Glycol + Potasium Carbonate at 298.15 K

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The salting effect on the liquid-liquid equilibrium (LLE) of organic aqueous solutions could be applied to many fields in the chemical industry, such as recycling of an organic solvent in a mixed solvent system and design of extractors. In the literature, the LLE data for the organic solvent + water + salt systems have been reported by some researchers, but as far as we know there is no report about LLE data for the system water + triethylene glycol + potassium Carbonate. In this work liquid-liquid equilibrium was determined for the system water + triethylene glycol + potassium Carbonate at 298.15 K. The experimental data was correlated using the improved regular solution theory. The general form of this model is as follows

$$\frac{\Delta G}{RT} = \left(\sum_i n_i \ln \phi_i\right) + \left(\sum_i n_i V_i\right)\left(\sum_i \sum_j A_j \phi_i \phi_j\right) - \frac{V}{4\pi a^3}\left[\ln(1+\kappa a) - \kappa a + \frac{(\kappa a)^2}{2}\right]$$

The parameters V_2, V_3, A_{12} and A_{13} for the system water (1) + triethylene glycol (2) + potassium Carbonate (3) were obtained from binary systems data. The parameter A_{23} is iterated from one set of conjugated LLE data of ternary system. The correlated accuracies with these parameters in term of average absolute deviation are less than 1%.

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Energy Functions of Liquid Multicomponent Systems, Treated by the Site-Site-Ornstein-Zernike Approximation

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The Helmholtz-Energy and the chemical potentials of the components in liquid multicomponent mixtures are derived with the help of the system of site-site-Ornstein-Zernike equations in HNC-approximation. The corresponding internal energies and the pair correlation functions are compared with results from Monte Carlo simulations.

Thermodynamics of Protein – Protein Interactions that Drive Bacterial Cell Death

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The principal decision of each cell is to choose between life and death. An "addiction module" is a genetically well-designed simple "biological bomb" that enables the cell to make such decision at definite times and under particular physiological conditions. The choice of life over the "default" death requires a dynamic antagonistic process manifested either by the continued production of the unstable anti-toxin or by a process that would prevent the degradation of the unstable anti-toxin. Therefore, cell death could be caused by anything that would prevent the continuous expression of the anti-toxic protein, or would increase the rate of its degradation. It seems that the suicide machinery in bacterial cells is always present and it only requires a trigger to activate it.[1]

We would like to understand better this machinery on the molecular level by characterizing the intra- (stabilities of proteins) and inter-molecular interactions (protein-protein, protein-DNA) within the addiction modules. This work is focussed on interactions that drive folding/unfolding of the intrinsically flexible addiction antitoxin MazE and interactions that are responsible for specific recognition of the DNA gyrase by the addiction toxin CcdB. The thermodynamics of interactions was studied by calorimetric and spectroscopic techniques and discussed in terms of the available 3D structures.[2-4] The obtained information was used in an attempt to predict some functional features of the addiction modules from the equilibrium thermodynamic model, which involves antitoxin and toxin molecules and DNA.

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Effect of Lanthanide Contraction on the Bonding in Octakis(Dimethyl Sulfoxide) Lanthanoid(III) Complexes

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All crystal structures studied in octakis(dimethyl sulfoxide)lanthanoid(III) iodides comprise discrete $[Ln(dmso)_8]^{3+}$ complexes surrounded by iodide ions. The $[Ln(dmso)_8]I_3$ (Ln = Sm, Gd, Er and Lu) compounds were characterized in the monoclinic space group $P2_1/n$, while the $[La(dmso)_8]I_3$ and $[Pr(dmso)_8]I_3$ structures crystallize in the orthorhombic P*bca* space group. The mean M-O bond distances decrease, 2.456(11), 2.431(7), 2.400(7), 2.383(7), 2.337(9) and 2.302(6) Å, for M = La, Pr, Sm, Gd, Er and Lu, respectively, as also the corresponding M-O-S bond angles, 139.2(7), 138.1(5), 137.5(5), 135.1(5), 132.9(6) and 132.5(3)^o. Correlations with the M-O bond length indicate a break in the trends between the praseodymium(III) and samarium(III) solvates, probably due to more efficient packing for the orthorhombic structures. Normal coordinate analysis of the vibrational spectra of the octakis(dimethyl sulfoxide)metal complexes were performed with full assignments of the vibrational frequencis. Substantial changes occur when the dimethyl sulfoxide molecule is coordinated, but the changes induced by varying the central ion in the lanthanoid(III) series are much less pronounced. The M-O stretching frequencies change most, and the M-O force constants increase smoothly with decreasing M-O distances. However, the increase is less for the smallest lanthanoid(III) ions, probably reflecting the effect of steric repulsion between the bulky ligands. The results were compared with the corresponding data obtained for the nonahydrated lanthanoid(III) trifluoromethanesulfonates,[1] for which the steric repulsion has more pronounced coordination effects.

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Database on Hydration Properties for Selected Aqueous Organic Solutes

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We have compiled and/or recomputed thermodynamic data from literature related to hydration process (Gibbs free energies and enthalpies of hydration enthalpies and hydration, partial molar heat capacities and volumes of solutes at infinite dilution,) for several classes of organic solutes (hydrocarbons, halogenated derivatives, oxygen and nitrogen containing compounds) at temperatures to 600 K and pressures to 40 MPa.

The original results directly related to experiments include Henry's law constants, limiting activity coefficients, phase equilibrium data, various reaction constants, enthalpies of solution, partial molar or apparent molar heat capacities and volumes. These values are complemented by auxiliary data on pure solutes such as vapour pressures, second virial coefficients and other pVT data, enthalpies of vaporization/sublimation and heat capacities in the ideal gas state.

Data from this collection are being used for the development of semi-theoretical prediction schemes for hydration properties in a wide range of temperatures and pressures.[1]

This and other databases such as collection[2] of the values at a reference condition of $T = 298$ K and $p = 0.1$ MPa serve as input for a broader data project, carried out under auspices of the International Union of Pure and Applied Chemistry (IUPAC) and the International Association for the Properties of Water and Steam (IAPWS). The objective is establishment of a database of recommended values on hydration properties for selected organic solutes at reference and elevated conditions ($T < 673$ K, $p < 40$ MPa,).

The purpose of this contribution is to provide a statistical overview of the database available at the Technical University of Liberec (presenting chemical structures, property types, temperature and pressure ranges) and it is useful for identification of solutes which can be candidates for inclusion in the collection of the recommended-values. Such an overview of available experimental data can be also instrumental for identifying chemical structures for which additional experimental effort in solution thermodynamics is needed.

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Conductometric Study of KBr in 2-Butanol + Water Mixtures

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Molar conductivity of KBr in 2-butanol + water mixtures, with alcohol mass fractions of 70, 80, 90 and 95 %, was determined at five temperatures in the range from 288.15 to 308.15 K. The limiting molar conductivity (Λ_o) and association constant (K_A) were calculated by the Lee-Wheaton equation[1] with parameter R set at q (Bjerrum's critical distance). The Walden product ($\Lambda_o\eta$) and the activation energy of the ionic movement ($\Delta H^{\ddagger}$), as well as the standard thermodynamic quantities for the association reaction, were derived from the temperature-dependent Λ_o and K_A, respectively. All quantities were compared with those obtained earlier for LiBr[2] and NaBr[3] in the same mixed solvent. Differences in the behaviour of cations were interpreted in terms of their size, as well as solvent basicity, structure and permittivity.

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Effect of Copper Oxidation State on the Properties of $CuCl_x$– MCl – H_2O Systems

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Effect of heterovalent metal oxidation state on the solution properties is one of the less studied problems of the Solution Chemistry. The main reason for this situation is that the metals which complexes with the same ligands have relatively high stability both in reduced and in oxidized form are rather rare. Copper allows the unique opportunity to undertake this type of investigation. Moreover, multicomponent systems containing copper complexes are of great importance in many fields of application, for example, they serve as photosensitive agents in photochromic and non-linear optics, catalyze many reactions of industrial and biological importance etc. Copper serves in electron transfer and catalysis of redox processes with a number of organic molecules; among them such organic reactions as decomposition of diazocompounds in the presence of sulfur-containing heterocycles, formation of S-yilides, oxidation of sulfides, etc. The variation of dominating copper species by change of solvents, ligands and outer-sphere ions can allow substantial increases of the efficiency and selectivity of copper-catalyzed reactions. In this report the results of investigation of multicomponent $CuCl_x$ – MCl – H_2O systems (x = 1, 2; $M^+ = Li^+ – Cs^+$, NH_4^+) are presented. The wide systematic study of solutions and solid compounds using solubility, dilatometry, vibrational spectroscopy and X-ray analysis was undertaken. The next aspects are under discussion

1. effect of alkaline chlorides on the solution properties depending on the copper oxidation state;
2. correlation between eutonic concentrations and fields of the dominating of different processes in solutions;
3. change of copper species during "solution – solid" transformation;
4. effect of alkaline cation on structural and molecular properties of complex salts.

The results obtained show that strong complexation determines qualitative similarity between all the systems containing copper(I). Competition of complexation and MCl association in copper(II)-systems determines stronger difference between $CuCl_2$– MCl – H_2O systems.

Acknowledgement. INTAS (Programme of INTAS fellowships for young scientists, project 04-83-3830) and Ministry of Education and Science of Russian Federation (Programme,"Development of scientificpotential of higher school", grant 37849) are thanked for the financial support of this project.

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Competitive Binding of Some Antibiotics within the Minor-Groove of DNA

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Recent development of organic synthesis of DNA directed drugs and availability of structural information on their complexes with DNA oligomers has set the stage for a detailed thermodynamic analysis of drug-DNA interactions that is of both practical and fundamental interest. Thermodynamics offers key insight into the molecular forces that drive the drug-DNA associations and cannot be estimated from structural or computational analysis alone. In addition to the contribution that thermodynamics can make on the practical level in terms of the rational design of DNA targeted drugs its fundamental interest is focused on the determination and prediction of the thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$, $\Delta C_P°$) that characterize various types of drug-DNA interactions.[1]

The motivation to study the competitive binding of the minor-grove directed antibiotics arises from our preliminary binding experiments performed with natural DNA, which show, that distamycin-A interferes with the binding of another antibiotic DAPI. To describe the DNA-sequence dependent molecular mechanism of competitive binding of some minor-grove directed antibiotics to the model DNA oligomers we employed spectrofluorimetric, spectropolarimetric, spectrophotometric and isothermal calorimetric titrations. Model analysis of the measured signals was applied to describe the binding within the measured oligomers in terms of populations of various species present in the solution.

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Application of the PFP-Theory to Excess Molar Volumes of Binary Mixtures of Acetonitrile + Ethers at Different Temperatures and Atmospheric Pressure

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As continuation of our study of excess molar volume of binary mixtures containing acetonitrile,[1-6] in this work excess molar volume of acetonitrile + tetrahidrofurane, or + 1,4-dioxane, or + diisopropyl ether have been determined, under atmospheric pressure as a function of composition and temperature. The temperatures studied were 288.15, 293.15, 298.15 and 303.15 K. The excess molar volumes were determined from the densities of pure liquid and mixtures using a vibrating-tube densimeter manufactured by Anton Paar (Model DMA 4500). The Prigogine-Flory-Patterson (PFP) Theory has been used to analyze the binary mixtures. The results of the calculations are discussed.

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Volumetric Properties of Binary Mixtures of Acetonitrile-Alcohol at Different Temperatures and Atmospheric Pressure

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Much effort in the determination of partial molar properties at infinite dilution has been used to obtain information about solute-solvent interactions, because at the limit of infinite dilutions, the solute-solvent interactions disappear.

In this work, excess molar volumes data of binary mixtures of acetonitrile + methanol, or + ethanol, or + 1-propanol, or + 1-butanol as a function of composition, under atmospheric pressure and at 288.15, 293.15, 298.15 and 303.15 K have been used to calculate the partial molar volumes at dilution infinite of each component using three different methods. The partial molar volumes at dilution infinite were calculated using the extrapolation of the Redlich-Kister relation, through the extrapolation of the apparent molar volumes and using a method based on extrapolation of the reduced volume. The results of these calculations are discussed.

Excess Molar Enthalpy of Binary Mixtures Containing Acetonitrile and Alcohol. Experimental Results and Modelling Using PFP Theory

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As continuation of our experimental study and modelling of excess properties,[1-6] in this work excess molar enthalpies ($H_{\mathrm{m}}^{\mathrm{E}}$) of binary mixtures of acetonitrile + heptanol, or + octanol under atmospheric pressure and at 298.15, 313.15 and 323.15 K have been determined. The excess molar enthalpies were measured using a modified Paar 1455 solution calorimeter (Parr Instrument Company). Both systems exhibit positive $H_{\mathrm{m}}^{\mathrm{E}}$ values over the whole mole fraction range in the temperature range studied and also it was observed that the excess enthalpies increase with the length of the alcohol chain and with increasing of temperature. The Prigogine-Flory-Patterson (PFP Theory) have been applied to correlate the present binary mixtures. The results of the calculations are discussed.

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Excess Molar Volumes of Binary Mixtures of Trichloromethane + Amines at Different Temperatures and Atmospheric Pressure

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As a continuation of our experimental studies on excess properties of binary mixtures of non-electrolytes, in this work excess molar volumes (V_m^E) data of binary mixtures of trichloromethane + n-butylamine, or + s-butylamine, or + diethylamine, or + triethylamine at 288.15, 293.15, 298.15 and 303.15 K have been determined. The excess molar volumes were determined from the densities of pure liquid and mixtures using a vibrating-tube densimeter manufactured by Anton Paar (Model DMA 4500). For all systems, V_m^E are negative over the whole mole fraction range in the temperatures studied and also it was observed that V_m^E values decrease with increasing of temperature. The experimental V_m^E decrease in the sequence: triethylamine < diethylamine < s-butylamine < n-butylamine. The V_m^E results are explained in terms of structural effects and complex formation between the components present in the mixtures.

Thermodynamics of Dissociation and Solvation of Valine in H_2O - PrOH-2. Temperature Dependence and Mathematical Modeling of Solvent Parameters. Relevant Contribution to the Alpha-Amino Acid Solvation in H_2O-MeOH, H_2O-EtOH, H_2O-PrOH-2.

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For the profound knowledge of biological system vital activity it is necessary to study biochemical reactions on the basis of quantitative analysis of chemical reactions in these systems. Extraordinary complexity of biological structures and functions requires the application of methodological principles of modern thermodynamics. Therefore the revealing of media (solvent) role in biological processes is the main problem of today solution chemistry that also determines the progress in such areas as molecular biophysics, molecular biochemistry, bioinorganic and bioorganic chemistry.[1] The basis for the selectivity of protein channels study and testing of corresponding theoretical assumptions are the thermodynamic data.[2] The aim of this work is revealing of regularities of connection between the thermodynamics of processes and energetics of solvation of reagents in amino acid solutions.

Thermodynamic constants of amino acid dissociation with carboxylic, K_1, and amino groups, K_2, and standard thermodynamic functions of dissociation ($\Delta G^0_{d,1}$, $\Delta G^0_{d,2}$, $\Delta H^0_{d,1}$, $\Delta H^0_{d,2}$, $\Delta S^0_{d,1}$, $\Delta S^0_{d,2}$) of valine have been determined in propan-2-ol-water solvent (0, 20, 40, 60, 80 % wt) by potentiometric method in galvanic cells without liquid junction:

Gl. el. (H^+) / $Z^\pm$ (m_1), HCl (m_2) / AgCl, Ag (I);
Gl. el. (H^+) / $Z^\pm$ (m_1), NaOH (m_2), NaCl (m_3) / AgCl, Ag (II)

at 278.15-328.15 K (with step of 10 K). The same functions are obtained for glycine and β-alanine in methanol-water (0, 20, 40, 60, 80, 95 % wt) at 278.15-318.15 K (with step of 5 K), α- alanine and valine in methanol-water (0, 20, 40, 60, 80 % wt) at 278.15-318.15 K (with step of 5 K), for glycine (278.15-318.15 K with step of 5 K) and α-alanine, β-alanine in propan-2-ol-water (0, 20, 40, 60, 80 % wt) at 278.15-328.15 K (with step of 10 K). The data on glycine and α-alanine in ethanol-water system at 298.15 K at I=0.1 mol/l are known from literature (0-60% wt and 0-80% wt accordingly).

The transfer Gibbs energy of the ionic forms of glycine, α-alanine and valine: protonated (H_2Z^+), zwitterionic ($HZ^\pm$) and deprotonated (Z^-) in methanol-water, propanol-2-water and of glycine and α-alanine in ethanol-water systems have been evaluated using our and literature data on $\Delta G^0_{d,1}$ and $\Delta G^0_{d,2}$. The change of the $\Delta G^0_{t,i}$ of amino acid ions and the short-range interaction part of dissociation Gibbs energy, $\Delta G_{d,1,2}^*$, obtained assuming the borders of ionic association area of amino acid have been generalized and analyzed as a dependence from solvent basicity and amino acid parameters.

Multiple regression analysis of water-organic solvent effect of water-methanol, water-ethanol, water-propan-2-ol on α-alanine and of water-methanol, water-propan-2-ol on valine strength at 298,15 K is provided. Energetic contributions of acceptor $\Delta\Delta G_{d,1}(E_T^N)$ and cohesion $\Delta\Delta G_{d,1}(\delta^2_N)$ properties of water-organic solvents into amino acid strength with carboxylic groups change $\Delta\Delta G_{d,1}$, and energetic contributions of acceptor $\Delta\Delta G_{d,2}(E_T^N)$, cohesion $\Delta\Delta G_{d,2}(\delta^2_{N.})$ and dielectric $\Delta\Delta G_{d,2}$ (ε_N^{-1}) properties of water-organic solvents into amino acid strength with amino groups change $\Delta\Delta G_{d,2}$ are evaluated. Contribution of electrostatic Coulombic interactions reveals itself only by dissociation of zwitterionic form of amino acid. Dissociation constants of cationic amino acids (as well as for other cationic acids from literary data) depend on solvent basicity, rather than on media dielectric properties. With exception of valine dissociation with amino groups in propan-2-ol-water, amino acid strength change (change in $\Delta G_{d,1}$ and $\Delta G_{d,2}$) is determined by cohesion interactions contribution. Amino acid dipole moment has been shown to be a meaningful parameter common for α- and β-amino acids. The data obtained in dilute region will permit to study inter particle interactions in concentrated amino acids solutions necessary to reveal the connection between thermodynamic and microscopic level for amino acid solutions.

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Measurement of Infinite Dilution Activity Coefficients of 1-Alkanols (C1-C5) in Water as a Function of Temperature

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Aqueous solutions of lower 1-alkanols have been of great interest for experimental thermodynamicists over a number of decades and, as a result, relatively abundant data on vapor-liquid equilibrium and other properties of these solutions are now available. However, while the existing equilibrium data are in a reasonable agreement for concentrated solutions, in the region of high dilution they are considerably scattered. In addition, the question of serviceable equation for temperature dependence of limiting activity coefficients (γ_1^∞) of alkanols in water has not been satisfactorily resolved yet.

In this work, limiting activity coefficients of lower (C1 – C5) 1-alkanols in water were measured as a function of temperature covering the range from the freezing to the normal boiling point of water. Six, well-established experimental techniques, namely headspace analysis,[1] inert gas stripping,[2] comparative tensimetry,[3] Rayleigh distillation,[4] non-steady-state gas-liquid chromatography,[5] and the method of circulation still,[6] were employed for the purpose. To establish reliable temperature dependence of γ_1^∞ for each of the systems, careful goal-directed measurements were carried out applying the methods alternatively, in accordance with the applicability conditions. About 15 new experimental values of γ_1^∞ were determined for each 1-alkanol. The method-to-method accord of the results, their thermo-dynamic consistency with calorimetric data on related thermal properties (limiting partial molar excess enthalpy $\bar{H}_1^{E,\infty}$ and heat capacity $\bar{C}_{P,1}^{E,\infty}$) and their accuracy were verified using two procedures. Experimental results were adequately represented by the following equation

$\ln\gamma_1^\infty = A + B/\tau + (C/\tau)\exp(D\tau)$, where $\tau = T/T_0$ and $T_0 = 298.15\ \mathrm{K}$,

whose parameters were reported for each of the 1-alkanol + water system studied.

Newly measured data greatly improve our knowledge of thermodynamic behavior of highly dilute solutions of 1-alkanols in water, opening possibilities for its more general treatment and detailed theoretical analysis. In addition, these results contribute to establishement of a data base on hydration properties of organic nonelectrolytes within an international project (2005 – 2007) conducted under auspices of IUPAC and IAPWS.

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Determination of Solvent Activity in Poly Ethylene Glycol Monomethyl Ether + Methanol, + Ethanol, + 2-Propanol and + 1-Butanol Solutions at 25 °C

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Phase equilibria plays an important role in the processing and application of polymers. In this respect, a quantitative description of the vapor-liquid equilibria (VLE) behavior in solvent + polymer systems is often necessary in order to design a polymer manufacturing process or to predict process performance. The solutions of poly ethylene glycol monomethyl ether with alcohols has been suggested as a working fluids in heat pups. In this work, the activities of methanol, ethanol, 2-propanol and 1-butanol in poly ehylene glycol monomethyl ether propylene glycol (M_p: 350) solutions have been measured by the isopiestic method at 25 °C. Sodium iodide and calcium chloride were used as the isopiestic standards for the calculation of activities. The original equation of Flory-Huggins and the modified Flory-Huggins equation with concentration dependent interaction parameters have been used for the correlation of obtained experimental solvent activity data. Better agreement with the experimental data was obtained using the modified Flory-Huggins equation.

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Complexation of Tungsten(VI) with Ethylenediaminediacetic Acid at Different Ionic Strengths

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The solution equilibrium of tungsten(VI) complex formed by ethylenediaminediacetic acid (EDDA) has been investigated potentiometrically and spectrophotometrically at 25 ^{o}C, pH = 7.5 and different ionic strengths ranging from (0.1 to1.0) mol dm^{-3} of sodium perchlorate. Tungsten(VI) forms a mononuclear complex with EDDA of the type (WO_3L^{2-}). The dependence of dissociation and stability constants on the ionic strength is described by a modified Debye-Huckel equation and introducing two empirical parameters. Finally a comparison has been made between the calculated and experimental values of stability constants.[1-3]

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Thermodynamic Study of Complex Formation of Nicotinamide with Ag^+ in Water-Organic Media

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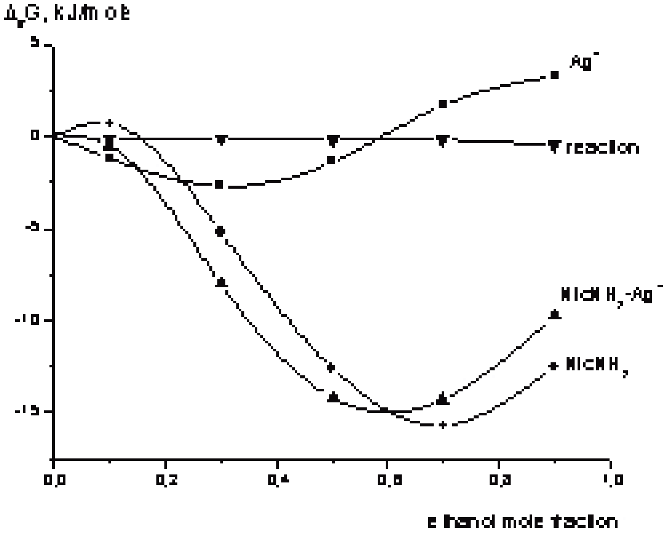
The ultimate goal of this study is to investigate the influence of water-ethanol and water-dimethylsulfoxide (DMSO) solvents on the complex formation of nicotinamide with Ag+. Nicotinamide is the PP vitamin. Silver is known to be the essential biologically active microelement and the efficient antiseptic. DMSO finds the application in medicine and biology, owing its ability for a rapid penetration through biologic membranes. Consideration both metal – macro natural molecules and metal – small biologically active molecules interactions needs to take into account structural and various physical-chemical properties of the processes media. In this study potentiometry was used by applying specially constructed electrode system. It included the pair of silver-sensitive electrodes of the first kind. The data on partition coefficients and turbidimetry was used to calculate Gibbs free energy values of transfer (ΔtrG) of nicotinamide from aqueous solution to the water-ethanol mixtures.

Experimental results indicate two clear alternatives: i) increase of lgK(NicNH2-Ag+) vs. ethanol mole fraction, ii) decrease of lgK(NicNH2-Ag+) vs. DMSO mole fraction. It can be assumed that till the mol fraction of ethanol 0.3 the Ag+ ion is principally hydrated. Above this point free Gibbs energy of Ag+ transfer increases. This gives the evidence about the weak solvation influence of ethanol on the Ag+ ions. The transfer of Ag+ from water to water-DMSO is accompanied by the depletion of the cation transfer Gibbs energy. Apparently, the Ag+-DMSO interactions considerably affect the value of the AgNicNH2+ stability constant.

Nicotinamide transfer from water to water-ethanol mixture implies the stabilization of the solvation state of the ligand. This may be the result of the dispersion interaction of the ligand molecule heterocycle with the solvent and of the influence of the amide group solvation peculiarities.

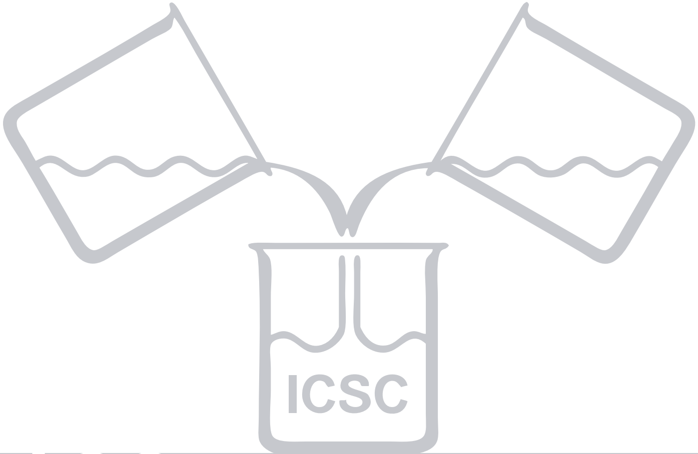
Relatively full thermodynamic analysis of the system under investigation is possible applying the well known equation: ΔtrG (reaction) = ΔtrG (NicNH2-Ag+) – ΔtrG(Ag+) - ΔtrG (NicNH2). Here is the graphic interpretation of NicNH2-Ag+ complexation thermodynamics in water and its mixtures with ethanol:



B.

POLYMERYS, COLLOIDS, INTERFACES AND MEMBRANES

Oral Presentations



Effect of Ion Association on Ionic Conductivity in "Soggy Sand" Electrolytes

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"Soggy sand" electrolytes are a new class of soft matter electrolytes obtained via Heterogeneous doping[1] of non-aqueous liquid electrolytes. Combination of high ionic conductivity and advantageous soft matter texture of the electrolyte makes them highly suitable for application in electrochemical devices e.g. lithium battery. These new soft matter electrolytes typically comprise of dispersions of solid insulating particles like SiO_2, Al_2O_3 etc. (size ~ 10-260nm, including mesoporous particles, average pore size: 3-6 nm) in liquid non-aqueous Li-salt solutions (e.g. LiCl, $LiClO_4$ in MeOH, THF[2] etc. or commercial solutions $LiPF_6$ in EC:DMC[3]). At oxide contents where the above composites represent a percolative network ("soggy sand" regime, figure 1), remarkably high ionic conductivities[2] compared to the pure solution were obtained. The enhancement is attributed to the adsorption of the anions on the oxides´ surface leading to dissociation of Li^+ out of ion pairs (high $[Li^+]$ in the vicinity of the oxide surface). Zeta potential measurements show that oxides are negatively charged and hence have adsorbed anions. Apart from various oxide particle parameters like surface activity, size, volume fraction etc, the conductivity enhancement is heavily dependent on degree of ion association in solution and in a way dependent on solvent parameter e.g. dielectric constant, viscosity and Li-salt concentration.

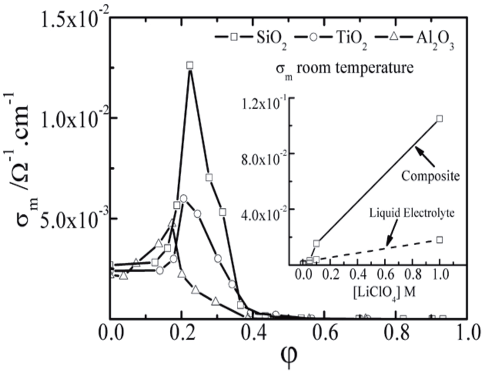

Figure 1: Variation of composite ionic conductivity (σm) versus volume fraction (ϕ) dispersed with various oxides (2r ~ 290nm) in 0.1 M LiClO4:MeOH solution (T=250C). Inset: σm versus [LiClO4] (SiO2 loading ϕ = 0.28)

We present here a systematic study of the effect of ion association on ionic conductivity in "soggy sand" electrolytes. Ionic conductivity (from ac-impedance) of dispersions of SiO_2 in non-aqueous LiCl/$LiClO_4$-S (S: EC, DMC, EC-DMC mixtures, THF etc.) was measured as a function of solution parameters e.g. solvent dielectric constant ($\varepsilon \approx 3$-90) , salt concentration ($c \approx 10^{-5}$ – 1 M), oxide size and concentration and temperature. Composite ionic conductivity is discussed including the critical role of triple ion formation for solvent $\varepsilon < 10$ (figure 2). Spectroscopic techniques like Raman, EXAFS etc. were also employed to study ion association and supplement ionic conductivity study. Theoretical explanation of ion conduction in "soggy sand" electrolytes uses the concept of Heterogeneous doping (applied to ceramic systems) together with theories of ion association in solutions.

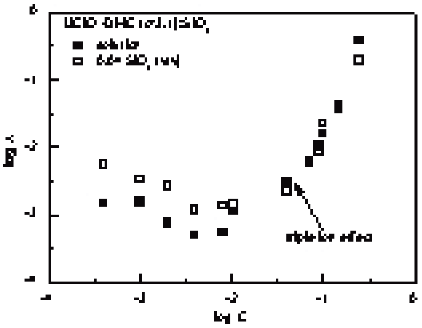

Figure 2: Variation of molar conductivity (Λ) versus [LiClO4] in solution (LiClO4: DMC) and composite with SiO2 (2r ~ 10nm) showing the triple ion effect.

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Partitioning Equilibria in Polymer and Colloid Solutions

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The equilibrium distribution of polymers between a solution and a porous material is a central mechanism in a variety of separation methods including chromatography and membrane-based processes such as ultrafiltration. Furthermore, the partitioning data are exploited to asses the depletion force between large colloid particles in presence of polymers and thus the phase stability of a mixture. To understand these processes, the dependence of the partition coefficient K ought to be explored on a variety of parameters such as sizes of pores and polymer solutes, thermodynamic quality of a solvent and the solute concentration, presence of attraction (adsorption) of polymers on the pore or particle surfaces, etc.

The results of the methodical study of partitioning of flexible macromolecules by molecular simulations will be summarized in the presentation. In contrast to ideal chain partitioning determined solely by the solute-to-pore size ratio, the partitioning rules in real systems are much more complex. The partition coefficient K increases with the solute concentration; rate of this enhancement is proportional to the polymer-solvent osmotic virial coefficient A_2.[1] The pore surfaces are often attractive to polymer segments and separation then proceeds by the mixed mechanism of steric confinement and wall attraction. Simulations properly reproduce[2] all three liquid chromatography regimes (around, below and above the critical point of adsorption ε_c) including the critical chromatography. Since both solute concentration and pore attraction enhance the partitioning coefficient K, the resolving power of nonideal partitioning decreases relative to the case of ideal chain partitioning.

Widespread industrial and biological applications of colloidal suspensions rest on a complex type of interparticle forces including depletion interactions. We have explored how the depletion forces (induced by polymer partitioning) are affected by the polymer concentration[3] and by weak attraction between polymers and particle surfaces.[4] The quantities of vital interest in colloidal stabilization such as the pressure exerted by the confined molecules on the particle walls and the effective depletion potential W(D) were calculated as a function of particle separation D and the attraction strength. It was found that the range and the depth of depletion interaction is reduced by an increase in the attraction and completely vanishes around the critical condition. It was concluded that an adjustment of polymer/particle interaction may represent an effective way of fine-tuning of the phase behavior of colloid-polymer mixtures.

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Imposing Dirichlet Boundary Condition on Closed Ionic Systems Containing Inhomogeneous Dielectrics. Application in Monte Carlo Simulations of Electrical Double Layers

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For decades, a central problem of computer simulations of ionic systems has been to correctly handle electrostatics. Problems usually arise from the unavoidable fact that the simulation cell is necessarily finite and that the electrostatic interactions are long ranged. Several methods (such as various summation techniques) to take into account long range corrections of charges outside the central simulation cell have been proposed using periodic boundary conditions, which are generally used to mimic a macroscopic sample.

We propose an alternative route which assumes a finite simulation cell confined by surfaces for which various boundary conditions can be applied. Dirichlet boundary conditions impose a prescribed potential on the confining surfaces (which we call electrodes). The boundary conditions are satisfied by placing an appropriate spatially-inhomogeneous surface charge (the electrode charge) on the electrodes. We propose a numerical procedure that enables the calculation of this electrode charge in every simulation step by solving a matrix equation. In this approach, the effect of the charges outside the simulation cell is no longer a consideration. The region outside the central cell is isolated from the cell by the Dirichlet boundary; the boundary condition implicitly contains the effect of the outside world. The method can be coupled to calculations of polarization charges induced on dielectric boundaries.[1]

The advantages of this approach are manyfold: (1) The electrostatics is correctly treated in a framework that is the natural choice for small finite systems. (2) If dielectric boundaries are present, the dielectric polarization charges induced by ions may harm the condition of electroneutrality. In this approach, the appropriate amount of electrode charge is induced on the Dirichlet boundaries and overall charge neutrality is automatically maintained. (3) In some cases, this geometry is closer to experimental situations. The best example is the electrical double layer, which is formed at the interface of an electrolyte and an electrode. The model that underlies most theories of the electrochemical double layer as well as earlier simulation studies assumes that the electrolyte (which is modelled as hard sphere ions solvated in a continuum solvent) is in contact with a hard wall carrying uniform surface charge and that the dielectric constant of the electrode is the same as that of the solution. In reality, the electrode is a metal and the surface charge is nonuniform. Furthermore, it is usually the voltage rather than the charge that is fixed.

In this contribution, we present our methodology, report Monte Carlo results on the electrochemical double layer in this new framework. We work in a planar geometry, namely, the system is infinite in two dimensions and it is confined by infinite planes (the electrodes) in the third dimension. We compare our results to those obtained in the traditional approach.

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Experimental Determination of Fe(III), Cr(III), and Th(IV) Polynuclear Hydroxo Complexes Composition

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At present, it is well established that hydrolysis of cations in solution proceeds in two stages with formation of mono- and polynuclear hydroxo species.[1] The first stage of this process – the formation of mononuclear hydroxo complexes - is relatively well studied. Much less is known about the formation of polynuclear hydroxocomplexes in solution. Though the fact of polynuclear hydroxo complexes formation and conditions for their formation are established for a series of metal ions, there are still a lot of discrepancies in the literature concerning their composition, stability and structure.

A methodological approach, allowing direct experimental determination of the composition of polynuclear hydroxo complexes, is proposed in the current publication. This approach involves a combination of several independent methods:

Determination of the polymerisation degree

The equations for two methods dialysis and spectrophotometry allowing determination of polymerisation degree have been calculated.[2] It has been shown that under the conditions investigated only binuclear hydroxocomplexes of Fe(III) and Th(IV) occur in solution, which is in a good agreement with the literature data.[3]

Determination of OH/Me ratio in polynuclear hydroxo complex

The OH/Me ratio was determined applying a pH metric titration method.[2] The results obtained indicated that in a case of Th(IV) OH/Me ratio in the polynuclear hydroxo complexes is about 3.9, i.e. the composition of dimmer is $Th_2(OH)_{7.8}{}^{0.2+}$

Determination of polynuclear hydroxo complex charge

This method is based on the fact that some anions can join polynuclear hydroxo complexes in solution without ousting OH-groups from the co-ordination sphere of the metal.[5] With an increase of anion concentration up to a certain point, the charge of the polynuclear complex is neutralised by the anion joined. Marking the anion with a proper radioactive tracer and applying dialysis method it is possible to determine the quantity of the anion bound to polynuclear hydroxo species of a metal.

The charge of Fe(III) polynuclear hydroxo complex was determined with the use of iodate and phosphate anion. Preliminary, it has been shown that both anions join polynuclear species of iron not changing their OH/Me ratio. The composition of the complex, according to the data obtained, is $Fe_2(OH)_{5.2\text{-}5.8}{}^{0.2\text{-}0.8+}$.

Similar results were also obtained in the case of Cr(III). The charge of its polynuclear species, which has been determined with the use of phosphate anion, was also in the range +0.2-0.8.

So, applying the above three methods the composition of polynuclear hydroxo complexes of Fe(III), Cr(III) and Th(IV) was studied. According to the data, obtained by all of the methods, the following species form in solution:

$Fe_2(OH)_{5.2\text{-}5.8}{}^{0.2\text{-}0.8+}$; $Cr_2(OH)_{5.2\text{-}5.8}{}^{0.2\text{-}0.8+}$ and $Th_2(OH)_{7.8}{}^{0.2+}$

According to a present conception,[5] the species forming at the first stage of cation polymerisation have a high positive charge the value of which depends on the charge of a cation hydrolysed – the higher is the charge of a cation the higher should be the charge of its polymers. However, the results obtained in the current work indicate that this conception is not applicable, at least, for the above mentioned cations. Therefore, it needs a further critical evaluation.

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Colloidal Suspensions: Equation of State

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The equation of state (pressure as a function of density) in suspensions of charged colloids is examined. Different approximations are compared and discussed. One of the surprising results is that calculation of the pressure based on the cell model almost exactly agrees with the primitive model Monte Carlo simulations for high and intermediate density regimes. Adding a colloid-colloid term at lower densities makes the cell approach working fine even there. Different routes to obtain the equation of state, namely the compressibility route and the virial route are also discussed and analysed.

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Dissection of Energetics of Micelle Formation

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The hydrophobic effect plays a key role in protein folding, protein-protein and protein-small molecule binding, protein-DNA and small molecule-DNA binding, membrane and micelle formation… Its temperature dependence is reflected in the corresponding changes of Gibbs free energy, $\Delta G°$, enthalpy, $\Delta H°$, entropy $\Delta S°$ and heat capacity, $\Delta C_P°$. For this reason calorimetric methods that directly measure the enthalpy changes resulting from various association/dissociation and folding/unfolding processes are essential for a successful thermodynamic analysis of these events.

In this work we measured the heat effects that accompany micelle formation of a series of model non-ionic surfactants in aqueous solutions by isothermal titration and differential scanning calorimetry. The concentration and temperature dependence of calorimetric signals were described in terms of populations of surfactant molecules in the monomeric and micellar macro state.[1]

In an attempt to characterize the molecular forces that drive the micelle formation the corresponding thermodynamic quantities will be discussed in terms of various contributions arising from the solute-solute and solute-solvent interactions. The motivation for such dissection of $\Delta G°$ originates from our recent successful attempts of parsing $\Delta G°$ accompanying protein unfolding/folding,[2,3] protein-protein binding[3] and drug-DNA binding events.[4] In all these cases the contribution to $\Delta G°$ due the changes in hydrophobic hydration was significant.

To correlate thermodynamics of micellization to the micelle structure in the solution the changes in the solvent accessible surface, ΔSASA, upon micelle formation areas were estimated from the corresponding experimentally determined enthalpies, $\Delta H°$, and heat capacities, $\Delta C_P°$, using the parametrization introduced by Murphy and Freire.[5] The resulting ΔSASA values are consistent with the micellar shape and size estimated by small angle X-ray scattering.[6]

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New Insights into Interactions between Hydrated Insoluble Polyelectrolyte and Weak Electrolytes

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Fully functionalized and cross-linked (to a certain degree) polyelectrolytes (styrene-divinylbenzene co-polymer for example, SDB) represent a group of insoluble ion exchangers, extremely important in research and industrial applications.

Such an example is the applications of those compounds as ion exchangers in modern ion chromatography.[1,3] A very special branch of modern ion chromatography represents Ion Exclusion Chromatography (IEC) in which some relatively weak acids (pKa>2) are separating on strong cation exchangers of very high capacity. The first publication describing this approach was published in 1953 by Bauman et all.[4] Since its introduction the theory of IEC has been continuously upgraded, but not significantly changed. The technique has been described by a variety of names, reflecting some uncertainty in the proposed basic separation mechanism. The currently held separation mechanism is based on two phenomena i.e. Donnan exclusion and hydrophobic interactions of the analyte with the stationary phase.

Although the current IEC mechanism is well elaborated and mathematically described, it still cannot give an appropriate answer to many questions regarding the phenomena observed in an IEC separation procedure, as for example (i) do Donnan exclusion and hydrophobic effects really make the major contribution to the overall efficiency of IEC separation?, (ii) what is the mechanism for the appearance of system peaks in IEC?, (iii) what are the reasons for the difference in peak shapes obtained in water or acidic eluents?, (iv) what is the mechanism in which an organic solvent and/or temperature influence the interaction intensity (retention time)?, (v) why are electrolytes having similar pK_a eluted at different retention times?, etc..

In the presented publication some experimental data will be present which are supporting the idea that the currently valid interaction mechanism between a weak electrolyte and a fully functionalized strong cation exchanger, should be re-evaluated. Based on the obtained experimental evidence, a completely new model will be proposed.

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Organization of Solvent Molecules Near Metal Surfaces - First Principle and MD Studies

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The structure and dynamics of solvent molecules on metal surfaces or near to metal surfaces in solutions have been at the focus of interest for decades. New phenomena, however, keep emerging due to improved experimental tools. Recently, in an scanning tunnelling microscopy (STM) experiment Mitsui et al.[1] directly tracked the motion of individual water monomers and small water clusters on Pd(111) surface. A most striking finding was that at 40 K water dimers diffuse much faster than the monomers. A cyclic $(H2O)_6$ the basic building block of Ih ice, was observed. A mechanism for the fast diffusion of water dimmers on metal surfaces was proposed, based on the ability of H-bonds to rearrange through quantum tunneling.[2]

In order to study the phenomena, the adsorption and diffusion of solvent molecules, - water, methanol, formaldehyde and formic acid molecules -, on Pd(111) surface has been studied with ab initio calculations and molecular dynamics simulations. The computational approach used is based on accurate quantum-mechanical calculations within the DFT formalism. The majority of the calculations are performed in periodically repeating supercells, which is most appropriate for studying extended systems like the Pd(111) surface. Core electrons are described through pseudopotentials. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation was used throughout.

Both the energetics and vibrational dynamics indicate the existence of well-ordered bilayer of water molecules on the surface. In addition, our calculation identifies two different hydrogen bonds in the bilayer. Both can be directly recognized from the vibrational spectra of the OH stretch modes. A novel diffusion mechanism of water dimers on metal surfaces has been proposed. Behaviour of methanol, and formic acid solvent molecules on Pd(111) surface, compared to water molecules, will also be discussed.

To study the structure and dynamics of water molecules near Pd(111) surface in solution phase extensive molecular dynamics simulations, based on ab initio potential energy surfaces, were carried out in order to follow the adsorption, clustering, diffusion of water molecules near palladium surface. After the introduction of the model potential energy surfaces, we shall demonstrate the results of the MD simulations in determining structure, stability, and the dynamical behaviour of water molecules near to Pd(111) surface. . High abundance of water pentamers near to palladium surface in solution was obtained and relatively fast diffusion of dimers was found from the MD simulations. In addition, diffusion activation energy determination and diffusion mechanism for dimers will also be discussed.

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Dielectric Discontinuity Effects in Suspensions of Charged Colloid

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For simplicity, the relative permittivity of colloids such as latex particles, surfactant micelles, or globular proteins is often treated to be equal to that of the surrounding solution. The relative permittivity could be as low as 2-5 in colloids formed by hydrocarbons, but believed to be somewhat larger in globular proteins. In aqueous solution at a room temperature, the relative permittivity is ca. 80. Only a few simulation studies have addressed how the distribution of counterions near a single charged colloid is affected by a low relative permittivity of the colloid.[1-3]

In the present work, we have studied how the effective interaction (the potential of mean force) between two macroions in an aqueous solution was affected by a low colloidal relative permittivity using Monte Carlo simulations. In more detail, two colloids, modeled as charged hard spheres, and their counterions were confined in a cylindrical cell.[4] The macroions were positioned on the principal axis of the cylindrical cell. The dielectric discontinuity was placed at the surface of the colloids, a position that gives rise to the largest effect. Technically, the dielectric discontinuity was handled by the so-called image charge approximation plus a truncated sum.

Our results show that the dielectric discontinuity in the model system introduces a repulsive force, which reduces the accumulation of the counterions near the colloid. This reduced electrostatic screening acts as a repulsive contribution to the potential of mean force between macroions and making the gas-liquid phase instability to appear at a significantly larger electrostatic coupling.

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Dynamic and Structural Properties of Inhomogeneous region at Solid-Liquid Interface

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The inhomogeneous region forming in the liquid near solid-liquid interfaces is studied by molecular dynamics computer simulations. While the structural properties, namely the density profiles and molecular orientation at the interface, are commonly explored for a number of systems, the determination of dynamic properties is less frequently performed. We will present the results on diffusivity profiles of water molecules next to a smooth and structured surface as a function of interaction potential and temperature. We will also present results on space-dependent viscosity calculation of Lennard-Jones fluid next to a smooth and structured surface, with comparison of equilibrium and non-equilibrium approaches and discussion of problems encountered.

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Structure of Aggregates and Viscosity of Some Mixed Surfactant Solutions Exhibiting Synergistic Effects

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The properties of a surfactant solution can change significantly on addition of other surfactants or low molecular substances. In some cases synergistic effects are observed being reflected in a decrease of the surface tension and critical micelle concentration, growth of aggregates and viscosity, peculiar features of the phase behavior etc.[1] Mixed surfactant solutions exhibiting synergistic effects are paid much attention during last decades and find numerous applications in detergency, pharmacy, food, chemical and oil industries etc.

The paper reports results of experimental measurements and computer simulations for 1) aqueous mixtures of sodium dodecylsulfate SDS (anionic surfactant) and alkyldimethyl amine oxide C_nAO, n=12, 16 (semipolar surfactant which becomes protonated in acidic solutions) and 2) solutions of cetyltrimethylammonium bromide CTAB (cationic surfactant) containing sodium benzoate (NaBenz) and 2-propanol (2-PrOH) as additives. The data on CMC, phase boundaries, viscosity and the size of aggregates (from dynamic light scattering, DLS) are presented in their dependence on the composition of the mixtures. It has been found that the viscosity of SDS - CnAO solutions depends significantly on the total and relative surfactant content, and on the acidity of the solution. Viscoelastic behavior was observed at some compositions. The concentration dependences registered for the average hydrodynamic radius and for the viscosity are in good agreement and give evidence of strong synergistic effects in aqueous mixtures of SDS- C_nAO. These effects are especially pronounced for mixtures enriched in C_nAO at natural acidity, and for 1:1 mixtures at low pH. Formation of mixed complexes in the system is confirmed by our previous data on the solution-solid phase equilibrium.[2]

According to the viscosity and DLS data, addition of NaBenz to solutions of CTAB results in the growth of micelles. The effects are even more pronounced in the case of mixed 2-PrOH+NaBenz additive though individual 2-PrOH is not effective. Detailed information on the structure of spherical and cylindrical micelles of CTAB in water or in water+additive mixture was obtained from molecular dynamics simulations. Density profiles for various atomic groups and radial distribution functions show significant penetration of benzoate counterions and water and propanol molecules inside micelles. The calculated structural properties and mobility of surfactant molecular fragments correlate well with NMR data and help in interpreting synergistic effects produced by the mixed additive.

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Cellular Automata Approach to the Role of Composition Inhomogeneitites and Diffusion in the Solution Side of the Interface with a Corroding Material.

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In our recent paper[1] we use the cellular automata based approach to simulate the development of the corrosion damage starting from a single punctual defect in the overall insulating and protective layer covering the material. Our simulations are similar in spirit to several models of this type known from the literature.[2-5] However we seem to have captured the essential features of the well known phenomenology of pitting corrosion[6] on iron, steel aluminium and similar materials.

This phenomenology states that once depassivated the material surface is liable to anodic dissolution. The anodic solution is acidic and rich in harmful anions. It prevents repassivation and promotes depassivation. In contrast the basic solution produced in the cathodic reaction is generally protective for the passive layer. Thus the spatial separation of anodic and cathodic reactions is advantageous from the point of view of the corrosion process. Here we show that this phenomenology is indeed sufficient to explain the pit initiation at a planar corroding surface and our model permits to study the peculiar role of diffusion in this important phenomenon.

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Electrochemical and Ellipsometric Study of Polypyrrol Films in Solutions Containing Ascorbic Acid

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Modified electrodes with electroactive polymers are relevant in sensors, microelectronic devices and analytical displays. Electrochemical and optical techniques has been applied to analyze the structure and the stability of polypyrrol (Ppy) films in the presence of dopamine (DA) and ascorbic acid (AA) in aqueous solutions.

Ppy shows high selectivity for the detection of the neurotransmitter dopamine DA, owing to the exclusion of anionic species by the negative charges in the film. The permeability of the film is particularly advantageous because the neurotransmitter is a cation.[1]

Ppy thin films are electrochemically grown on gold electrodes in 0.25 M K_2HPO_4, 0.25 M KH_2PO_4 buffer solutions by anodic polarization.[2] Several voltammetric perturbations are applied during the electropolymerization process studying the effect of both different scan potential rates and different ageing times.
Ellipsometry is applied in situ to characterize the film grown on the specular polished gold substrate. The optical indices of the Ppy film, n - i k, are calculated in the 405 nm < □ < 580 nm spectral range using the gradient technique.[3] The refraction index, 1.40 < n < 1.55, and the absorption index 0.07 < k < 0.11 and the thickness d, 10 nm < d < 450 nm were calculated.[4]

A slow increase in d and a concomitantly decrease in n – i k are detected at open circuit conditions in the presence of AA. This is related to a partial inclusion of solvent that takes place together with anion uptake processes after AA addition in the buffered solution. After several hours the thickness may twice the size of the initially deposited layer. The DA concentration is related to the pseudocapacitive response of the redox couple, Q, of the neurotransmitter that permeate through the film. The measured thickness d, voltammetric charge, Q, electrode potential and optical constants, n, k, depends on both the permeability of AA and DA species and the compactness of the polymeric Ppy layer. The correlation among these parameters for the different electrodeposited Ppy layers allows progress toward a deep microscopic insight on the interfacial zone and on the processes taking place during the current detection.

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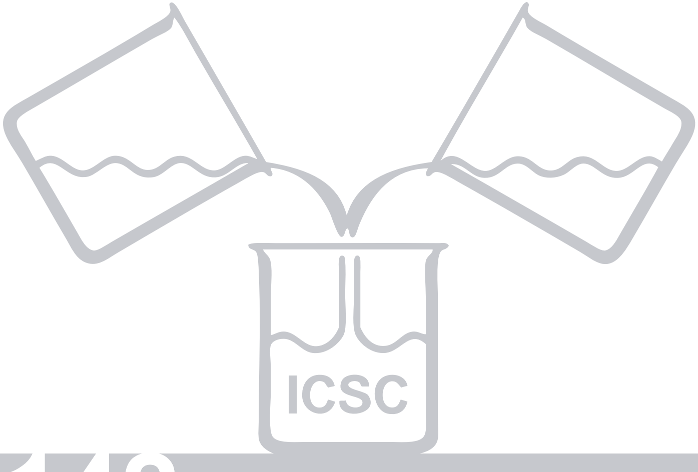
B.

POLYMERYS, COLLOIDS, INTERFACES, AND MEMBRANES

Poster Presentations



Partitioning of a Cationic Surfactant into Giant Phospholipid Vesicles

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The partitioning of a cationic surfactant cetylpyridinium chloride, CPC, into giant lipid vesicles prepared from 1-palmitoyl-2-oleoyl-phosphatidylcholine, POPC, was examined at various lipid concentrations ranging from 0.79 to 7.3×10^{-6} mol/L. Unilamellar lipid vesicles with sizes up to 100 μm were prepared by an electroformation method. The lipid concentration in vesicle suspensions was determined by a spectrophotometric method. The potentiometric method based on surfactant-selective electrode was used for the determination of surfactant concentration in the external solution. The concentration of surfactant incorporated into vesicles was calculated by taking into account the volume of the lipid phase. From these data, the amount of surfactant incorporated in the membrane per mole of lipid (parameter β)[1-3] and the partition coefficient K_c[2,3] were calculated. Two distinctive linear regions were identified in binding plots (i.e. β vs. concentration of CPC in external solution) at low surfactant concentrations. From the slopes of these linear regions, the effective partition coefficients $K_{S,1}$ and $K_{S,2}$ were determined.[3,4] The values of K_c, $K_{S,1}$ and $K_{S,2}$ were found to be considerably larger than the available literature data for other studied surfactants and pointed to a high tendency of CPC to incorporate into POPC vesicles. This finding was attributed to the size of vesicles on one hand and to the geometric characteristics of the CPC and POPC molecules on the other.[1] The surfactant-induced changes of vesicle shape were followed by optical microscopy and were related to the concentration dependence of K_c. The results indicated a three stage process of solubilisation of lipid vesicles by CPC. First, stable vesicles with mixed bilayers form, which become saturated with CPC at a value β_{sat} which is larger than 0.8, and then gradually disintegrate. This is accompanied by a decrease in K_c from values larger than 1×10^6 to around 1×10^4. Just prior to the break-down of the vesicles, formation of ellipsoidal vesicle shapes was noticed. This phenomenon was attributed to the cooperative incorporation of surfactant into the bilayer. The second stage, extending over a broad region of surfactant concentrations from around 1×10^{-5} mol/L to around 1×10^{-3} mol/L, is characterized by almost constant K_c values and corresponds to the region where myelin-like bilayer structures were observed. Fluorescence measurements have shown that the second stage in the solubilization process of POPC by CPC does not involve mixed micelles as usually proposed in such studies.[3] Instead, vesicles gradually transform into less regular bilayer structures, while the formation of mixed micelles is limited to the third stage of the solubilization process.[2,5] In this stage, a sharp increase in K_c is noticed, which is ascribed to mixed micelle formation. The corresponding critical micellization concentration, CMC, decreases with increasing concentration of the lipid.

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Electrochemical Formation and Degradation of Polyaniline on Titanium and Niobium Electrodes

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The polymerization of aniline on a titanium and niobium electrodes in aqueous sulfuric acid solutions with various concentrations of added aniline has been studied employing in-situ electrochemical and Raman spectroscopical techniques.[1,2] Aniline was polymerized by cyclic voltammetry utilizing a more cathodic potential range (up to –0.6 V sce) for the cyclisation than is usual (up to –0.2 V sce) on Pt and Au electrodes. For limit cathodic potential of –0.2 V sce the mechanism of electro-synthesis on a Ti and Nb electrode is similar to that on a Pt and Au electrodes. For cathodic potentials more negative than –0.2 V sce the new peaks, indicating change in mechanism of electro-polymerization were detected.

On fig.1. the voltammograms on Nb electrode recorded after multi-cycle scans indicated complex redox processes occurred on electrode surface during the film thickness growth. The regular increasing anodic and cathodic current of each successive cycle reflects the regular growth of the polymer film. The cathodic peak F1 for the first time has been monitored on Nb electrode. This peak only appears if cyclic voltammetry, measurements are performed with higher anodic potential limits through the peak D, i.e. with formation of degradation products (peaks B-B1 and C-C1)[3]

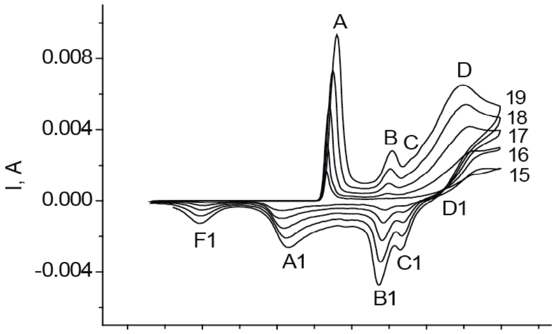

Fig.1. Cyclic voltammograms 15 to 19 cycles recorded on Nb support that the polymer electrode in 1M H2SO4 + 0,1 M aniline added. (v = 20 mV/s)

Tentative assignments of Raman bands provide chain consists: para -di substituted benzene rings, semi-quinone radical cations, benzoquinone, hydraquinone, p-amino-phenol, quinoneimine, and quinoid diradical di-cations.

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Solutions of Oligoions: A Computer Simulation Study

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Charged oligomers play important role in several industrial and biological systems. One example are polyamines which determine higher-order DNA structure.[1,2] In industrial applications short polyions are often used as bridging agents in colloidal phase separations. These systems occupy important region of molecular masses between the low-molecular electrolytes on one side, and polyelectrolyte solutions on the other. Here we propose a model that mimics short flexible macromolecules which may be fully or only partly charged. To model oligoelectrolyte solution the oligoions are represented as charged hard–sphere chains where some (or all) monomer units (beads) carry a charge. The corresponding small spherical ions (counterions), distributed in the solution, neutralize the charge on the polymer chains. Aqueous solutions containing these flexible (chainlike) oligoions have been studied using the canonical Monte Carlo simulation technique. Oligoions are assumed to be formed from beads which are modeled as hard spheres with radius of 2 Å. The beads (4, 8, or 16 of them) are tangentially bonded to form an oligoion. The charges are located in centers of beads and interact with counterions via the Coulomb potential; the solvent is in majority of calculations treated as continuous dielectric. No angular potential has been applied. Beads can be either charged with one elementary charge or neutral. In this calculation we varied the charge on each oligoion from 25% to 100% (every bead is charged) by mixing the appropriate numbers of charged and neutral beads on the oligoion. In few calculations we relaxed the primitive model approximation and treated the solvent molecules as neutral hard spheres with a radius of 4 Å. The number of oligomers in a typical computer simulation was from 40 to 80. We will present structure of the solution by a set of radial distribution functions between different species. Among the thermodynamic quantities excess internal energy and chemical potential of water will be calculated. The results will be compared with theoretical predictions based on the theoretical approach called "product reactant" Ornstein–Zernike theory developed by Kalyuzhnyi, Stell, Blum, and others.[3-5]

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Interaction between Charged Planar Surfaces Mediated by Divalent Rod-Like Ions

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We consider interactions between identical like-charged planar surfaces in aqueous multivalent salt solution. Attractive interactions between identical like-charged surfaces arise due to ion-ion correlations. The mean-field level Poisson-Boltzmann theory does not predict such behaviour for point-like structureless ions. Various multivalent ions, such as certain DNA condensing agents do have an internal, often rod-like, structure. Applying PB theory to the generic case of divalent rod-like salt ions, we find attraction between like-charged macroions above a critical distance between the two individual charges of the rod-like ions. We calculate this distance analytically within linearized PB theory and numerically within non-linear PB theory.

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Thermodynamic Modeling of the Rheological Behavior of PEG3000 – PEG20000 Aqueous Solutions

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In this work a new model for calculating of dynamic viscosity of newtonian and non-newtonian polymer solutions previously developed by the authors is applied to aqueous polymeric systems (polyethylene glycol with nominal molecular weight 3000 g/mol, 6000 g/mol, 10000 g/mol and 20000 g/mol aqueous solutions). The model is based on Eyring absolute rate theory, and in the solution theory of McMillan-Mayer. An equation of state, as the Soave-Redlich-Kwong equation, is used for the calculation of the solution osmotic pressure, and so the excess molar McMillan-Mayer free energy. Therefore, an expression for the viscosity of a polymer solution can be written as direct function of the shear stress. The proposed model contains a term that describes the viscosity of a dilute newtonian solution, combined with a second term that describes the deviation from newtonian behavior, and with a third term that represents the deviation from the thermodynamic ideality.

The proposed model presents five adjustable parameters, one related to the conceptual model employed for the ideal solution, two of them (the parameters of the equation of state) are related to the deviation from the thermodynamic ideality, and the last two parameters are related to the deviation from newtonian behavior of the polymer solution.

In order to test the proposed model we have measured experimental rheological data for several polymer concentrations, at different shear stresses, at 298.15 K and 0.1 MPa. We have used a rheometer Haake RS1, with a titanium double gap coaxial cylindrical rotor (DIN53544). The shear stresses were scanned from 0.1 Pa up to the maximum supported by the system and the equipment.

The previously proposed model has been used for correlating the viscosity values in function of the applied shear stress and polymer solution concentration. It has been found that the agreement between the calculated values and experimental ones are within the experimental error of 2 %.

Analysis of Osmotic Pressure Data for Aqueous Protein Solutions Via a Multi-Component Model.

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Integral equations theory and Monte-Carlo simulations are used to study Donnan equilibrium, which is established by an equilibrium distribution of a simple electrolyte between an aqueous protein-electrolyte mixture and an aqueous solution of the same simple electrolyte, when these two phases are separated by a semi-permeable membrane. The polyelectrolyte solution is represented by a three-component mixture of charged hard spheres, which models aqueous solution of polyions (proteins), co-ions and counterions. In order to describe the unusually low osmotic pressure of these solutions the new model allows for dimerization of protein molecules. The associative mean spherical and hypernetted chain approximations were applied to this model. In addition the Monte Carlo computer simulations were performed for the same model. The model parameters were chosen to mimic solution of lysozyme in presence of 0.1M sodium chloride. The theory and simulations are found to be in good agreement for the thermodynamic properties as chemical potential and osmotic pressure under these conditions.

Using the theoretical approach mentioned above we analysed experimental data for the osmotic pressure of bovine serum albumin (BSA) in 0.15M sodium chloride[1], human serum albumin (HSA) solution in 0.1M phosphate buffer[2] and lysozyme in sulphate and phosphate buffers.[3,4] According to the previous experimental and theoretical study[2] the first two solutions differ substantially in the degree of protein association. The theoretically determined osmotic coefficient can be fitted to the experimental results to obtain the fraction of dimers in a solution. Our analysis indicates that there is relatively small self-association of protein molecules for BSA solutions at pH = 5.4 and 7.3, with fraction of dimers ≤ 10%. In the case of HSA solutions strong negative deviations from ideal value is found and at pH = 8.0 a reasonably good agreement between the theory and experiment is obtained by assuming full dimerization (100% pairing). For solutions with pH = 5.4 the best fit of experimental results is obtained for a fraction of dimers equal to 80%.

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Critical Micele Concentrations of some Cationic Surfactants in Sulfuric Acid as Obtained by the Electrochemical Method

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The critical micelle concentration (CMC) is the concentration in which the surfactant molecules in solution start to form aggregates. These aggregates also called colloidal micelles are formed from variable number of molecules, ranging from tens to hundreds of surfactant molecules. The formation of colloidal micelles depends on subtle equilibrium between the hydrophobic attraction of the carbon chains, accompanied by a reorganization of solvent molecules, and the repulsion between polar head.[1]

Critical micelle concentration is influenced by a series of factors that depend on the nature of the surfactant, the aqueous environment, and even on the method of determination used. Critical micelle concentrations can be determined by monitoring any physical property as a function of the surfactant concentration providing that the property changes substantially upon formation of micelles. In practice, osmotic pressure, surface tension, and electrical conductivity are the most often used methods.[2]

The use of surfactants as corrosion inhibitors is one of the most useful methods for protection against corrosion in acidic media. In this inhibition process critical micelle concentration is the most important parameter. When the concentration of surfactant adsorbed on the solid surface is high enough, the organized structures (the hemi-micelles such as bi - or multilayer) are formed; the process decreases the corrosion reaction by blocking the metallic surface.[3-9]

On the basis of kinetic parameters measured in corrosion processes, the CMC of chosen cationic surfactants of the type of N-alkyl quaternary ammonium salts in 2 M H_2SO_4 was estimated. For this purpose, a conventional three-electrode configuration was used for potentiodynamic studies. All the potentials were measured against the saturated calomel electrode (SCE) and the counter electrode was made from Pt. The experiments were carried at temperature 25°C ± 1°C. The potential was applied and controlled by SOLATRON 1287 Electrochemical Interface.

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Concentration of a Carbon-PTFE Dispersion by Phase Separation

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Gas diffusion electrode is widely used for a fuel cell and an oxygen cathode such as chlor-alkali membrane cell. The use of the oxygen cathode saves 1/3 of the power consumption of this process. Gas diffusion layer (GDL) of PEM fuel cell was prepared by dispersion of carbon black and PTFE in water with non-ionic surfactant such as Triton X-100. This dispersion has only 10 wt% solid composition. The much water must be removed in order to obtain the necessary film thickness. The water content wants to lower in order to improve the workability by simple method. Then, the cloud point of the surfactant property was noticed. It is well known to become hydrophobic property, when the surfactant is heated over the cloud point. The dispersion is separated to two phases of top and bottom. The upper part is thin, and the lower becomes thick. It is reported that the making process of the gas diffusion electrode using concentrated dispersion for the PEM fuel cell.

Triton X-100 is used as a non-ionic surfactant with 65.5 °C as the cloud point at 1 wt% aqueous solution. The carbon black is AB-6 (Denka Black, DENKIKAGAKU KOGYO, INC.), and polytetrafluoroethylene (PTFE) dispersion (Fluon AD911, ASAHI GLASS CO., LTD). The dispersions were contained with 7.8 wt% AB-6 and 5.2 wt% PTFE in water containing the 1~30 wt% non-ionic surfactant. The carbon black was mixed with pure water (milliQ, Millipore) containing Triton X-100. The dispersing carbon black mixed solution was dispersed a jet mill (Genus PY, GENUS Co., Ltd) at 100 MPa, and it is done 5 times. The particle size was measured in Fiber-Optics Particle Analyzer (FPAR 1000, Otsuka Electronics Co., Ltd). The average particle size of the carbon black in the dispersions was ca. 500nm. The temperature of the heat treatment are 65~85°C by 0.5 to 24 hr in water bath with a temperature accuracy of +/- 0.1°C. After heat treatment, the separated interface height of dispersion was measured. The concentration of the concentrated dispersion and the concentration of the surfactant were measured from the specific gravity. The water containing a few percent of Triton X-100 takes place 2 phases at upper 66 °C. In the 2 liquids region, it is divided into upper layer with the less concentrated region of Triton X-100 and lower layer with the more concentrated region of Triton X-100. The dispersion of carbon black and PTFE containing Triton X-100 was separated 2 liquids at upper temperature of the cloud point of Triton X-100 - H2O system. It is divided into upper layer with the less concentrated region of the total solid (carbon black and PTFE) and lower layer with the more concentrated region of the total solid.Many results were separated to dilute phase and thick phase. On certain conditions, the upper layer became a clear phase.

Figure 1 shows separation rate of the dispersion containing various percent of Triton X-100 at 69.0 °C. The separation rate depends on heat treatment temperature and concentration of Triton X-100 in the dispersion. The separation rate is dependent on the concentration of Triton X-100. It was the most quickly separated at 7 % TR dispersion. It proves that concentration dispersion with the solid (carbon black and PTFE) over 42 wt% was possible. The concentrated dispersion was diluted at original concentration again, and then, the particle size was measured. It was almost equal to the particle size before and after heat treatment.

A MEA was made using this concentrated dispersion on Al foil by application method. The gas diffusion electrode using the MEA was indicated good performance.

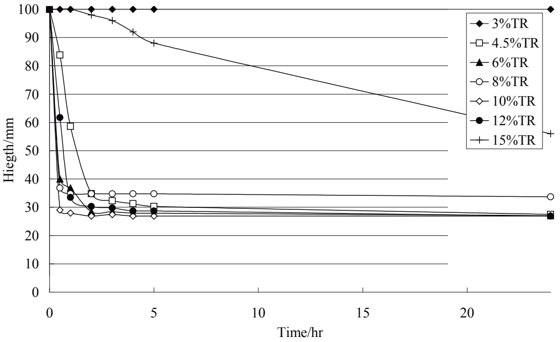

Fig.1. Separation rate of the dispersion containing various Triton X-100 concentrations at 69.0 °C.

Mechanism of Copper Dissolution in Ammonia Solutions

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The electrochemical behaviour of copper in ammonia-based solutions is very important for several industrial processes such as electroplating, etching etc. and has, thus, been studied quite extensively. However, a closer look reveals that most studies have suffered from rather low reproducibility of the results. Most probably, the low reproducibility has been due to numerous parameters influencing the corrosion mechanisms and, thus, have to be controlled appropriately. We will show on the example of cyclic voltammograms that with careful control of these parameters (pH, c(NH_3), c(Cu^{2+}), T), very reproducible results can be obtained. Combining electrochemical experiments with ex-situ IR spectroscopy and scanning electron microscopy, we propose a detailed mechanism of copper dissolution in ammonia solutions.

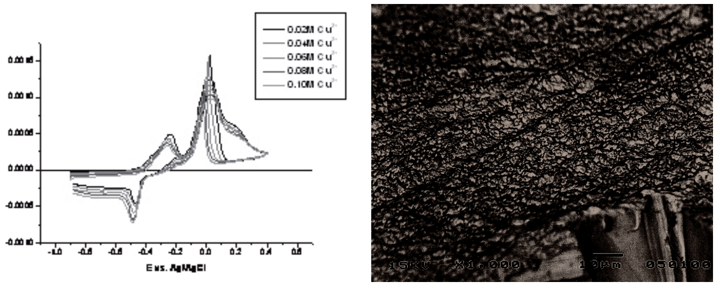

Figure1. Left: cyclic voltammograms of Cu in 1M NH_3 at different concentrations of Cu^{2+}. Right: SEM micrograph of passivated Cu at –0.2V vs. Ag/AgCl.

To check the validity of the proposed mechanism, we calculated the corresponding impedance spectra for different potential values and compared the calculated spectra with the measured ones. It turns out that, at least for this particular case, the impedance spectroscopy has a high resolving power revealing many details in the reaction mechanism.

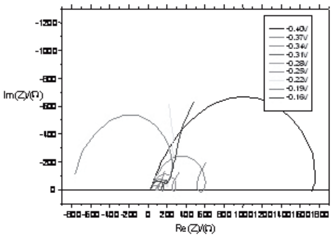

Figure 2. Impedance spectra of Cu in 1M NH_3 (pH=11.4) as a function of potential (vs. Ag/AgCl).

A Modified Free Volume-Based Model for Predicting Phase Equilibria of Polymer Solutions

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The purpose of this work is to present a combinatorial/free-volume term in predicting Vapor-Liquid Equilibrium (VLE) and Solid-Liquid Equilibrium (SLE) of polymer/solvent and hydrocarbon/hydrocarbon mixtures. The proposed term is based on a modification of the original Freed Flory-Huggins model, replacing the molar volume with a free-volume (FV) term. Using an extensive database for athermal polymer solutions at finite dilution, the single parameter of the model has been adjusted. The results obtained from the model peroposed in this work were favorably compared with those obtained from the well-established FV-models, i.e., the entropic-FV and the modified entropic-FV models.

We propose in this work a modified free-volume based Freed equation, hereafter termed Freed-FV:

$$\ln \gamma_1^{FV-comb.} = \ln \frac{\phi_1^{fv}}{x_1} + 1 - \frac{\phi_1^{fv}}{x_1} + \alpha (1 - \frac{v_1^{fv}}{v_2^{fv}})^2 (\phi_2^{fv})^2 \tag{1}$$

where $\phi_i^{fv} = \frac{x_i v_i^{fv}}{\sum_j x_j v_j^{fv}}$ and $v_i^{fv} = v_i - v_i^{vdW}$. The value of the universal adjustable parameter of the Freed-FV model, ie. α, has been set to 0.2, based on extensive database of polymer-solvent VLE including various temperatures and concentrations.

The following results obtained using the proposed model in comparison with the Entropic FV (EFV) model and the Modified Entropic FV (MEFV) models.

1. For athermal and non-athermal (with weak interactions) polymer-solvent systems, Freed-FV is as good as MEFV and EFV.
2. For highly polar systems, Freed-FV is as good as EFV, while MEFV fails, possibly because the modified hard core volume (1.2V_{vdW}) has been obtained for athermal mixtures. In the Freed-FV model the presence of the non-randomness parameter may explain the good results for these systems.
3. Freed-FV performs much better than both EFV and MEFV for infinite dilution activity coefficients of short-chain alkanes in long-chain ones (γ_1^∞) and long-chain alkanes in short-chain ones (γ_2^∞).
4. For SLE, the Freed-FV model provides much better results compared to the two other models, especially for asymmetric systems.

The comparison of the predicted results with experimental data for athermal systems containing polymer, light and heavy hydrocarbons (VLE and SLE) shows that the proposed model significantly corrects the underestimation of the original and modified entropic-FV models particullary in predicting the long-chain activity coefficient for asymmetric systems.

Heat of Ionization of Poly(L-glutamic Acid) in Aqueous Solutions

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The conformational changes of poly(L-glutamic acid) and its derivatives in various solvents and in the presence of added simple salts have been studied also by direct calorimetry.[1-6] In present work the enthalpy change accompanying the conformational transition of poly(L-glutamic acid) from helix to coil, $\Delta H_{conf,}$ has been determined from calorimetric titration curves, in which the dependence of the heat of ionization on the degree of ionization has been determined. The results of the measurements show that the enthalpy of the conformational transition depends on the polypeptide concentration. The values derived for 0.002 and 0.1 monomolar solutions are: $\Delta H_{conf} = (2.0 \pm 0.1)$ and (1.7 ± 0.1) kJ/mol, respectively. This finding has been supported by the heat of dilution measurements which display an unusual dependence on the degree of ionization, in sharp contrast to the behavior of other weak carboxylic polyelectrolytes. An endothermic heat effect has been detected in dilution process, which is superimposed on the exothermic enthalpy of dilution, and which overweights the latter in the region of α where the conformational transition is prevailing. For the dilution from the initial concentration 0.1 monomol dm^{-3} to the final concentration 0.002 monomol dm^{-3} the value of this endothermic heat effect is 220 J/mol, which is in rough agreement with the difference between the two values of ΔH_{conf} (0.3 kJ/mol) given above.

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Ion Binding with Heparin

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Influence of ionic strength on ion binding with heparin was investigated using a new radiochemical method. The method is based on Donnan equilibrium and an isotope exchange of counter ion between electrolyte and polyelctrolyte. An advantage of the method is a distinction between ions bound territorially and specifically.

At 310 K a degree of counter ions bound with heparin via non-specific electrostatic interactions was determined as function of ionic strength using electrolytes labeled with $^{36}Cl^-$. In the limit of zero ionic strength all counter ions are bound territorially with heparin. The association degree decreases linearly with the square root of the ionic strength. Isotope exchange of $^{22}Na^+$ between heparin sodium salt and NaCl showed that not all sodium ions are exchangeable, indicating that these ions can be bound specifically. In the limit of zero ionic strength a degree of locally bound sodium ions is about 0.45. This decreases rapidly with increasing ionic strength and becomes negligible when the ionic strength exceeds 0.01 M.

Probing Polymer Adsorption by Cell Adhesion

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Adsorption of biopolymers is probed by cell adhesion at the mercury electrode/aqueous solution interface using electrochemical technique - chronoamperometry. The surface charge density of mercury electrode immersed in an aqueous electrolyte solution can be finely tuned by controlling the electrode potential. We have previously shown that the signal frequency of cell adhesion is dependant on biopolymer surface concentration.[1,2]

Dextrans are known for their specific adsorption (displacement of water molecules and ions) at mercury electrode/aqueous solution interface in a range of positive but also negative surface charges.[3] Adsorption of dextran molecules is fast and controlled by mass transport from the solution. Dextran sulfate with average molecular weight of 500 000 was chosen as negatively charged biopolymer. On the other hand, unicellular marine algae Dunaliella tertiolecta (cell diameter 6-9 μm) can be characterized through their adhesion at mercury electrode that results in well-defined electrical attachment signals at millisecond time scale.[4]

For the given cell density frequency of cell adhesion decreases with the increase in surface coverage of dextran molecules. The extent of adsorption of dextran sulfate was probed at positively ($\sigma = +3.8\ \mu\mathrm{C\ cm^{-2}}$) and negatively ($\sigma = -6.5\ \mu\mathrm{C\ cm^{-2}}$) charged mercury electrode/ 0.1M NaCl solution interface. For dextran concentrations >50 mg $\mathrm{L^{-1}}$ cell adhesion was significantly suppressed only at positively charged mercury electrode. Our results clearly show the evidence of the electrostatic repulsion between dextran sulfate molecules and negatively charged mercury electrode.

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Simple Home Constructed Digital Image Processing System for Contact Angle Measurements

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An own on video image analysis based instrument for contact angle measurements has been developed. Contact angle (CA) characterizes the interfacial tension present between a solid, a liquid and a vapour phase. The technique provides a simple and fast method to generate a great amount of information for surface analysis.

A measurement system in composed of a metal framework holding a light source, a sample plate and a digital camera which is connected to a PC running digital image recognition software. The sample temperature is controlled by a water thermostate.

Our own image recognition software has been developed that detects edges (changes in gray level) on a digital image, identifies a surface contact line and a drop shape, while statistically filtering out bad edges. Surface base on which sample is placed is depicted by a straight line, while a drop shape is approximated by a circle obtained by a numerical regression procedure. A tangent line is constructed at a contact point between liquid drop and a surface material, and a contact angle determined (Fig. 1). The method provides contact angles accurate to ±0.2 degrees.

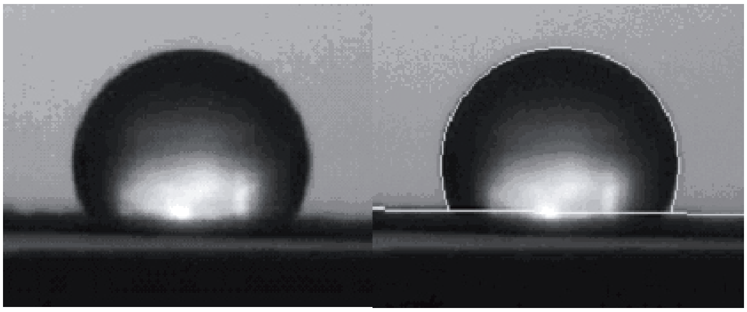

Figure 1. Images of a sessile drop of water on paper impregnated with footwear water repellent. Raw image (left) and analysed image (right) with a line representing the surface, and a curve of a recognized drop shape.

Above named accuracy, and good repeatability of results are maintained, if a special care is paid on how sample drop is deposited on a substrate. Different drop sizes, roughness and porosity of sample surfaces affects the angle slightly. In the cases where drops are attracted by a surface, a contact angle is diminishing during the measurement process. To compensate this, the value of the contact angle is extrapolated back to the time when drop was deposited on the surface.

The applicability of the developed method of CA measurements for different liquids on different substrates will be demonstrated.

Effect of Ionic Strength on Formation of Polyelectrolyte Complexes in Solution; A Comparison with Corresponding Polyelectrolyte Multilayers

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Mixing of aqueous solutions of positively and negatively charged polyelectrolytes results in formation of polyelectrolyte complexes, predominantly due to the electrostatic interactions between oppositely charged chains.[1] It is known that the presence of electrolytes and ionic strength influences the formation of such complexes. On the other hand, it has been shown recently that same factors significantly influence the process of formation and erosion of polyelectrolyte multilayers obtained by alternatingly dipping a substrate into, or flushing with, solutions that contain the negative and the positive polyelectrolyte, respectively.[2,3]

The influence of different salts (KCl, $NaNO_3$, Na_2HPO_4 + KH_2PO_4) and ionic strength on polyelectrolyte complexes formed by mixing aqueous solutions of poly(dimethylamino ethylmetacrylate) (PAMA) and polyacrylic acid (PAA) was investigated. The methods used for the investigation of complex formation were nephelometry, conductometry and electrophoretic light scattering. The obtained results were compared with results obtained by investigating the influence of different salts and ionic strength on multilayer formation process. These experiments were based on alternate adsorption of same polyelectrolytes (PAMA and PAA) on silica using stagnation point optical reflectometry method. It has been shown that the behavior of polyelectrolyte multilayers formed on metal oxides is governed by the same principles as that of corresponding polyelectrolyte complexes in solution.

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Osmotic Coefficients of Aqueous Ionene Fluoride Solutions

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Ionenes are strongly charged cationic polyelectrolytes whose charged groups are located on the polymer main chain. The aliphatic x,y-ionene is a compound which consists of specimens with different numbers (x,y) of methyl groups between the quaternized nitrogen atoms. The charge densities of these compounds can be varied in the synthesis by using appropriate reagents.[1]

Osmotic coefficients of aqueous solutions of 3,3-, 4,5-, 6,6-, and 6,9- ionenes with fluoride counterions were measured at 298 K and in the concentration range from 0.001 to 0.1 basemole/dm^3. The measured osmotic coefficients are low, indicating large deviations from ideality caused by strong interactions in these systems. The solutions with fluoride counterions have lower osmotic coefficient than the corresponding bromide solutions[2] which is in agreement with experimental data for the counterion activity coefficient of these solutions. The experimental results for osmotic coefficients were analyzed using a cylindrical cell model[3] where a fixed charge is assumed to be uniformly distributed along the z-axis of a rigid and impenetrable polyion, in conjuncture with the classical Poisson-Boltzmann equation.

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MD-Simulation on Microheterogeneous Water Structures in Mixtures of Aqueous N,N'-Methylenebisacrylamide-Crosslinked Poly(N-isopropylacrylamide) (P-NIPAM) with Acetonitrile

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The heterogeneity of the liquid water structure in presence of N,N'-methylenebisacrylamide (BIS)-crosslinked poly(N-isopropylacrylamide) (P-NIPAM) and (BIS)-crosslinked polyacrylamide (PAA) networks is caused by the different functional groups of the polymers, as it can be shown by MD-simulations. We examine methods of analysis for an extraction of local structure information in such complex fluids. In general, the local water structures can be roughly characterized by the radial distribution functions in terms of the classical site-site pair correlation. These simple functions indicates a strong anisotropy for water near the functional groups. By the use of angular dependent radial distribution functions, we accomplish a more thorough investigation of the local water structure and its microheterogeneity, induced by the presence of the polymer. Of particular interest are the water distribution at the crosslinkers. The strong electrostatic interactions between the competing functional groups and the water molecules is decisive for the formation of the structure. The angular resolved pair correlation functions allows us to calculate local coordination numbers and detailed information of the water distributions around the functional groups of the polymer network. The simulation results of the local dynamics indicate that the stability of the local water cluster in the polymer network is controlled by the local structure of the network. However, on the nanoscale, a significant dependence between the polymer concentration and the ensemble-averaged translational diffusion is missed. The averaged values of translational diffusion are in a good agreement with experimental results.[1] Our results yields an understanding of the permeability in the microheterogeneous interface between the crosslinked polymers and water.

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Differential Pulse and Square Waves Voltammetric Techniques as Useful Tools to Study the Colloidal Properties of Magnetic Fluids

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Electric Double Layered Magnetic Fluids (EDL-MF) are ultrastable colloidal dispersions of ferrite magnetic nanoparticles in aqueous medium and are currently used in the design of new magneto-pharmaceuticals. Recently, electrochemical techniques have been proposed to study the colloidal properties of EDL-MF and the pH-dependence of the surface charge density has been determined using simultaneous potentiometric and conductimetric measurements.[1,2] As surface ferric ions may undergo direct electrolysis, voltammetric techniques (VT) would allow investigations of redox processes of metal oxides, charge transfer mechanisms on chemically modified surface as well as adsorption processes. Moreover, the VT also permit quantitative studies, being sensitive even for very low concentrations (ppm and ppb ranges). In the present work we investigate EDL-MF based on cobalt ferrite nanoparticles using differential pulse and square waves VT. The measurements are carried out using a HMDE or glassy carbon working electrode, the Ag/AgCl reference and the Pt coil counter electrode in the range of +1.0 V to –1.0 V. The chosen supporting electrolyte is a HNO_3 10^{-3} mol L^{-1} solution using suitable aliquots of 15 μL of ferrofluid samples for several volume fractions of magnetic nanomaterial. In all curves, the observed peak at –0.55 V is assigned to the iron reduction of nanoparticle surface ions. When compared to the ferric ion peak lying at +0.48 V, the observed peak potential shift is due to the iron neighbouring of the particle surface. We also investigated the current response due to ferrofluid samples complexed by oxalic acid. In this case, the surface complexation induces a shift of the peak potential as observed for complexed ferric ion, towards to more negative potential (-0.70 V). In all our measurements, the peak current is proportional to the iron content of particles. The analysis of such results is made in terms of a faradaic process determined by the diffusion current of the electroactive species, according to the Nernst formalism. For the first time, voltammetric measurements have been used to characterize magnetic colloids and would enable a new approach to monitor the iron content in human blood samples in biomedical in vitro applications of biocompatible magnetic fluids, since the iron from the particles can be distinguished from that of the biological matrix.

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Correlation between Ketoprofene Release and the Structure of the Delivery System: SAXS, Conductivity and DSC Studies

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Colloidal drug delivery systems are important in a sense of improving the bioavailability of drugs. Microemulsions are dispersions of oil and water stabilized with a surface active film composed of surfactant and cosurfactant. They are of special interest in this context because of their spontaneous formation, thermodynamic stability and optical transparency.[1,2] As such they can serve as promising vehicles for administrating drugs. In this study, the microemulsion type and structure have been investigated by small-angle X-ray scattering (SAXS), electrical conductivity measurements and differential scanning calorimetry (DSC) on a dilution line containing, initially, 20 wt.% of isopropyl miristate (IPM) and 80 wt.% of the surfactant (Tween 40®)/co-surfactant (Imwitor 308®) mixture (1:1 wt.%). This initial mixture was then sequentially diluted with water. In order to lay the basis for predicting drug release under in vivo conditions, where the microemulsion composition is continuously varying, ketoprofene release was then measured for each type and structure.

By analysing samples with DSC changes in cooling curve can be observed. In combination with SAXS and conductivity data different types of the microemulsion were inferred. DSC and conductivity data showed that at the selected dilution line microemulsions containing less than ~ 20 wt.% of water were expected to be of W/O type. Microemulsions containing between 20 and 40 wt.% of water appeared as bicontinuous with both, water and oil as continuous phases. Finally, microemulsions containing more than 40 wt.% of water were expected to be of O/W type.[3] The results of SAXS experiments on the Tween/Imwitor/IPM/water system show that a very low scattering intensity for the samples without water is the most probably a consequence of a low contrast in the electron density of the dispersed scattering objects relative to the continuous phase.[4] The scattering increases significantly with the addition of only a small amount of water and keeps rising with further increase of water concentration. In parallel the scattering maxima gradually shift toward the smaller scattering angles indicating the growth of the scattering nanostructures. With the samples containing more than 50 wt.% of water a greater change in the course of the scattering function is observed. Quite pronounced and very sharp scattering maxima that develop on these scattering curves indicate the presence of the scattering structures that at least partially (or locally) adopt some higher level of order. The scattering curves clearly show two equidistant maxima, which is usually a signature for the presence of lamellar phases in the microemulsion systems.[5]

It was found that the main factor influencing ketoprofene release is shown to be the strength of the interactions between water and surfactants in microemulsion, which was detected by DSC measurements. Samples identified as having different structures show, with one exception (percolation range), different release profiles. In all cases, the release kinetics is of zero order indicating that the release rate is dependent on diffusion of ketoprofene inside the microemulsion carrier.[3]

The characterization of the nanostructures of microemulsions using different experimental methods thus enable us to predict the ketoprofene release from microemulsion as well as to get an insight into how a microemulsion might change its structure and therefore its ability to release ketoprofene upon entering a physiological environment.

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Osmotic Coefficients and Apparent Molar Volumes of Atactic and Syndiotactic Poly(methacrylic Acid) in Aqueous Solutions: Dependence on Degree of Neutralization

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Poly(methacrylic acid), PMA, is the simplest representative of a synthetic polyelectrolyte that can be prepared with a different degree and type of stereo-regularity. Solution properties of PMA depend on its stereo-regular structure. In this contribution, we report on the osmotic coefficient and apparent molar volume measurements for the atactic and syndiotactic forms of PMA, a-PMA and s-PMA, respectively. The atactic (sometimes referred to as the conventional) form of PMA was prepared by polymerization of methacrylic acid using a standard procedure. For the determination of tacticity, a-PMA was transformed into the ester form and the tacticity was determined from its ^{1}H NMR spectrum in $CDCl_3$. The content of traids was around 40% atactic, 50% syndiotactic, and 10% isotactic.[1] Syndiotactic PMA was prepared by the hydrolysis of syndiotactic poly(meth ylmethacrylate), s-PMMA, Polymer Source Inc., Canada, in concentrated sulphuric acid and was further purified by exhaustive dialysis against water. The polymer contained 85% of syndiotactic, 11% of atactic, and 4% of isotactic triads, as determined from the ^{1}H NMR spectrum of the starting s-PMMA.

Osmotic coefficients of a-PMA and s-PMA, neutralized with standard sodium hydroxide solution to provide several fixed degrees of neutralization, $\alpha_N = 0, 0.25, 0.49, 0.76$, and 1, were measured with a Knauer vapour pressure osmometer over a moderate concentration range. The results show that these two forms of PMA have a similar ability to bind sodium ions. This indicates that the molecular conformations of a-PMA and s-PMA chains in aqueous solutions are similar, in agreement with small-angle X-ray scattering data.[2] The values for the osmotic coefficients are in the same range as for other vinyl polyelectrolytes and increase with decreasing α_N.

The apparent molar volumes, Φ_v, were calculated from the measured densities of solutions for the same α_N values as osmotic coefficients. From the concentration dependence of Φ_v, the values of the apparent molar volume at infinite dilution, Φ_v^0, were obtained for each α_N. The Φ_v^0 values increase with decreasing α_N and are very similar for a-PMA and s-PMA, in agreement with osmotic coefficient measurements. The increase in Φ_v^0 is more rapid in the region $1 > \alpha_N > 0.4$, whereas for α_N below approximately 0.4, Φ_v^0 increases more slowly with decreasing ionization. The $\alpha_N <$ 0.4 range corresponds to the region where the pH-induced conformational transition of a-PMA and s-PMA (from a more extended conformation at high α_N values to a more compact form at low α_N) is observed in aqueous solutions.[3] By applying the additivity of the apparent molar volumes of ions at infinite dilution, the contribution of the polyion to the apparent molar volume of the polyelectrolyte was obtained in dependence on the degree of neutralization. The values for a-PMA and s-PMA were compared with the ones for the isotactic form of PMA.

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The Influence of the Electrolyte Composition on the Underpotential Deposition of Hydrogen on Gold

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As in the case of the gold oxide formation, there are three current voltammetric waves that can be attributed to the H UPD on the three main crystalline faces of the metal. The amount of deposited hydrogen is higher if the number of crystal defects is greater. The hydrogen atoms diffuse into the bulk metal. The resulting hydrogen coverage depends on the relative contribution of the forwards and backward diffusion steps. Moreover, the hydrogen adsorption is more evident on the less coordinated crystalline planes as the (110) and the (111) planes.

The hydrogen deposition can be obtained by over-potential[1] or by under-potential[2] cathodic electrolysis. In both cases the hydrogen atoms diffuse in to the bulk metal. Only adsorbed hydrogen atoms give a charge transfer reaction. As in the case of the platinum electrodes, the steps that contribute to the formation of adsorbed hydrogen atoms determines the measured current: a) Molecular hydrogen dissociative adsorption. b) Hydrogen atom surface recombination. c) Hydrogen atom diffusion in to the metal. d) Hydrogen atom diffusion out of the metal. e) Hydrogen ion electroreduction. f) Hydrogen atom electrooxidation. The steps c and d are not significative when the reaction takes place on platinum. The process is less reversible on gold because the contribution of steps c and d is important.

Taking account of these steps, a mechanism is postulated that reproduces the experimental behaviour. Two-compartment electrochemical cell is used. Spectroscopic pure gold wire and gold sheet is the working and the counter electrode respectively. A reversible hydrogen reference electrode is placed in a compartment connected to the main compartment through the Luggin capillary. Sulphuric and perchloric acid solutions are used as supporting electrolytes. Both are degassed with pure nitrogen and the cell is maintained under nitrogen atmosphere. All reagents are of analytical purity. The mass transfer is enhanced by controlled solution stirring.

The study with the perchloric acid solution clarifies the mechanism because perchlorate ions do not adsorb on the gold surface too extensively as the sulphate ions.

The potentiodynamic current/potential profiles are simpler in the case of the perchloric acid than in the case of the sulphuric acid and only one anodic current peak that can be attributed to the hydrogen atom oxidation clearly defines.

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Effect of Complexing Anions on Formation of Polynuclear Hydroxo Species of Cr(III) in Aqueous Solution

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At present, it is established that hydrolysis of cations in solution proceeds in two stages – formation of mononuclear hydroxocomplexes and formation of polynuclear hydroxocomplexes.[1] Currently, the first stage is relatively well studied in comparison with the second one. Though the fact of polynuclear hydroxocomplexes formation and conditions for their formation are established for a series of metal ions, the questions of polynuclear hydroxocomplexes composition, stability and structure are still not enough investigated. At the same time, such data are most interesting not only from scientific point of view but also for solution of practical problems. The effect of anions on hydrolysis of Cr^{3+}-cations with formation of polynuclear hydroxocomplexes was investigated applying a complex of physico-chemical methods: dialysis, ultrafiltration, centrifugation, pH-metric titration, method of radioactive indicators, spectrophotometry. A series of anions chosen for investigation included: iodide, iodate, phosphate, oxalate, and EDTA- anion. The results obtained allow one to make a conclusion that the effect of an anion depends on the stability of their complexes with Cr^{3+}-cations to their ability to form complexes with Cr^{3+}-cation. Thus, iodide anion, forming weak complexes with Cr^{3+}-cations, doesn't interact with polynuclear hydroxocomplexes of Cr(III) under all the conditions investigated. The effect of IO_3^- and PO_4^{3-}-anions is that they do not decrease the total content of polynuclear hydroxoforms in solution and are able to join Cr(III) polynuclear hydroxocomplexes, causing formation of bigger particles precipitated by centrifugation. Iodate anion, at lower concentrations (10^{-5} – 10^{-3} M), does not have any visible effect on the percent of Cr in a form of polynuclear species. The increase of the anion concentration higher than 10^{-3} M results in formation of bigger particles. In solution with 10^{-3} M of Cr(III) and 10^{-4} M of phosphate anion retention of phosphate by a semipermiable membrane begins at pH 4.5, which indicates that phosphate anions interact with the polynuclear species with formation of mixed hydroxo acido complexes. Nearly 100% of phosphates are retained in a range of concentrations 10^{-5} - $7 \cdot 10^{-4}$ M. At a higher concentration of the phosphate its retention is decreasing. This testifies to the fact that the charge of polynuclear species of Cr is neutralised at this point. Comparison of the data obtained within the current work with our previous data[2] show that the interaction of the above anions with polynuclear hydroxocomplexes proceeds in a similar way in the case of Cr(III) and Fe(III). The effect of oxalate- and EDTA-anions is determined by their high complexing ability with respect to Cr^{3+}-cation. These anions are able to hinder formation of polynuclear hydroxo species and decrease their content in solution down to a total cease of the polymerisation reaction, at higher concentrations. The mechanism of anions influence, resulting in hindering the formation of polynuclear hydroxocomplexes in solution, can be explained by ousting pH-groups from coordination sphere of Cr^{3+}-cation. As a result of it either acidocomplexes or mixed acidohydroxocomplexes with a number of pH-groups not sufficient for their participation in polymerization reactions are formed.

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Mutual Diffusion of Nonionic and Ionic Mixed Surfactants in Water: Effects of the Cross-Term Diffusion

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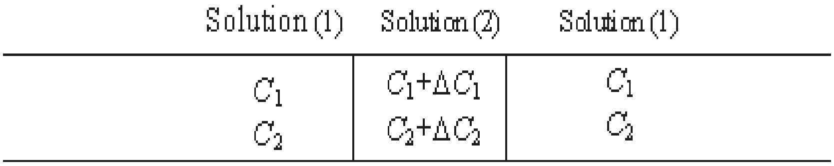
Mutual diffusion coefficients of both zwitterionic and nonionic surfactants increase significantly when long-chain ionic surfactants are added above critical micelle concentrations (CMCs) of the zwitterionic or nonionic surfactant.[1,2] In the case of ternary systems consisting of two solutes (components (1) and (2)) and solvent (component (0)), fluxes of components (1) and (2) are given as a function of the component's concentration gradients by

$$J_1 = -D_{11}\frac{\partial C_1}{\partial x} - D_{12}\frac{\partial C_2}{\partial x} \qquad (1) \qquad\qquad J_2 = -D_{21}\frac{\partial C_1}{\partial x} - D_{22}\frac{\partial C_2}{\partial x} \qquad (2)$$

where D_{11} and D_{22} are main diffusion coefficients and D_{12} and D_{21} are cross-term diffusion coefficients. Depending on the initial concentration gradient, the cross-term effect can be large. In this study, we have measured mutual diffusion coefficients for mixtures of nonionic and ionic surfactants above the CMC of the nonionic surfactant.

Diffusion coefficients were measured by the Taylor dispersion method. Specifically, 20µL of a solution (solution (2)) was injected into a solution (solution (1)) flowing through a capillary tube. At the end of the tube, concentration (refractivity) profile was detected by a differential refractometer.

When solution (1) is 10 mM octaethylene glycol monododecyl ether ($C_{12}E_8$, component (1)) + 1 mM octadecyltrimethylammonium chloride (C_{18}TACl, component (2)) (1 M = 1 mol dm^{-3}) and there is no initial concentration gradient for the component (1) ($C_{12}E_8$), the concentration (refractivity) profile at the end of the capillary was not a single but a double Gaussian curve, with the fast diffusivity component close to that for the (estimated) mutual diffusion coefficient of the C_{18}TACl + water binary system and the slow diffusivity component close to that of the $C_{12}E_8$ + water binary system. By making measurements with various initial ΔC_1 and ΔC_2, diffusion coefficients D_{ij} were calculated. One of the most remarkable results is that the cross-term value D_{12} is larger than the larger main value, D_{22}. This fact suggests that the solubilized $C_{18}TA^+$ ions, through electrostatic coupling with the counter ion (Cl^-), accelerate the low diffusivity of $C_{12}E_8$.



Solution (1)	Solution (2)	Solution (1)
C_1	$C_1+\Delta C_1$	C_1
C_2	$C_2+\Delta C_2$	C_2

Fig.1 Initial concentrations of component (1) (C1) and component (2) (C2).

When hexyltrimethylammonium bromide (C_6TABr) was used instead of C_{18}TACl with the initial ΔC_1 = 0, the concentration (refractivity) profile at the end of the capillary was single Gaussian, suggesting essentially no interaction between $C_{12}E_8$ and C_6TABr.

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Modeling of Water in Confined space

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Confined water can be found in many natural environments,[1,2] including those in biology. In pure liquid water at room temperature or below, water has extensive hydrogen bond network structure. But if water is confined between planes or in microscopic spherical or cylindrical pores, its structure and thermodynamic properties can be perturbed. Such confinement effects have been studied by experiments[3] and theory.[4]

In this contribution we present new calculations for a model of water in an external filed provided by confinement. We use a simple computational model, proposed originally by Ben-Naim,[5] to study the properties of water in confined spaces. Water molecules are modeled as two-dimensional (2D) Lennard - Jones disks, with three orientation-dependent hydrogen-bonding arms, arranged as in the Mercedes Benz (MB) logo. This model has previously[6] been shown to predict qualitatively the volume anomalies of pure water and the free energy, enthalpy and entropy, heat capacity and volume change for inserting a non-polar solute into water. In the present work, which is continuation of our studies of MB molecules in an environment that imposes steric constraints on the water molecules,[7] we study the MB model of water between two parallel Lennard-Jones adsorbing surfaces. For this purpose different Monte Carlo simulation methods, and a version of the density functional theory (DFT) suitable for systems with directional forces, were applied. We calculated the density profiles next to surfaces and the effect of external field provided by walls on the ability of molecules to form hydrogen bonds. The calculations were performed for different width of the micropore and at various temperatures. In the density-functional approach we applied an orientation-averaged level of the theory. The comparison of the density-functional theory results with computer simulations indicates that the theory provides semi-quantitatively correct description of the structural properties for the explored range of model parameters.

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Monte Carlo Simulation Study of the Double Layer of Asymmetric Electrolytes

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The primitive model of electrolytes assumes that the ions are modelled as charged hard spheres embedded in a continuum dielectric representing the solvent. The double layer formed at the interface of an electrolyte and an electrode. The electrode is commonly modelled as a hard wall carrying uniform surface charge. In the framework of this model, we report results for systems where we allow[1] the ions to have different valence and/or diameter,[2] the solvent to have a concentration dependent dielectric constant, and in some cases[3] the electrode to have a different dielectric constant from that of the electrolyte.

We use Monte Carlo simulations and report results for[1] the capacitance of the double layer as a function of the concentration,[2] and the dimensionless reduced temperature (the inverse of the coupling constant),[3] for the potential at the point of zero electrode charge (PZC), and for the charge-voltage relationship.

The temperature dependence of capacitance of the double layer is known to change sign according to ionic association. We show results for this phenomenon in the case 2:1 and 3:1 electrolytes. If we assume that the dielectric constant of the solution decreases with the increasing concentration, we can explain experimental behaviour commonly described by the Parsons-Zobel plot. Using domains of different dielectric constants near the interface is a commonly used assumption in explaining experimental data in the framework of the Gouy-Chapman theory. The validation of this approach with computer simulation is still a task to be accomplished. We report some results for the case where the dielectric constant of the electrode is infinite representing a metal.

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Use of Diafiltration to Evaluate the Interactions Between Polymers and Low Molecular-Weight Molecules in Solution

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The diafiltration technique has served to evaluate and quantify the interactions between water-soluble polymers (WSP) and low molecular-weight molecules (LMWM).[1-3] This technique is based on the separation of particles whose size is greater than the diafiltration membrane pores (as water-soluble polymers) from smaller molecules. The rate of filtration of the LMWM under the washing method (analogue to a Batch method) is strongly influenced by their interactions with the WSP. Dealing with polyelectrolytes, where electrostatic interactions are dominant, it is found that the total number of charges is the most important variable that determines the strength of the interaction, rather than the polymer structure itself. However, π–π interactions seem to play a crucial role in WSP-LMWM interactions when both the polymer and the LMWM bear aromatic rings. Both π–π and electrostatic interactions in water are sensitive to the addition of electrolytes as NaCl. As an example, the interactions between Rodamine B (RB) and poly(sodium 4-styrenesulfonate) (PSS) or poly(N-mathacryloyl-5-aminosalicylic acid) (poli(5-HMA)) are showed at different ionic strengths and pH values. The interactions are also followed spectroscopically by observing the quenching of RB fluorescence as a consequence of complex formation.

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Mixed Solutions of Isotactic Poly(methacrylic Acid) and Cetylpyridinium Chloride in Water: Cooperative Binding and Influence of Surfactant on the Conformational Transition of the Polyelectrolyte

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In this work, we have studied interaction of a cationic surfactant cetylpyridinium chloride, CPC, with a stereoregular form of poly(methacrylic acid), i.e. with isotactic poly(methacrylic acid), i-PMA. The sample of i-PMA contained 92% of isotactic, 4% of heterotactic, and 4% of syndiotactic triads and was insoluble in water up to the degree of neutralization, α_N, equal to approximately 0.2. Results for i-PMA were compared with those for the usual atactic PMA, a-PMA, with a triad content of 40% atactic, 50% syndiotactic and around 10% isotactic triads.[1]

Firstly, the effect of CPC on the solubility of i-PMA, on the degree of ionization, α, of carboxyl (COOH) groups, and on the conformational transition of the polymer was studied. The addition of CPC leads to the solubilization of un-neutralized i-PMA ($\alpha_N = 0$) when the molar ratio of CP^+ ions to COOH groups on PMA, denoted by S/P, reaches 0.4. Surfactant has a pronounced effect on the ionization of COOH groups: upon the addition of CPC, the degree of ionization of i-PMA increases by nearly 5-times at $\alpha_N = 0$ and by more than 20% at $\alpha_N = 0.1$. The addition of surfactant influences also the position of the conformation transition of i-PMA, which is induced by the ionization of COOH groups. In pure solutions of i-PMA, the conformational transition is observed in the region between $\alpha \approx 0.15$ and $\alpha \approx 0.40$, but is shifted to higher α in the presence of CPC; for S/P = 0.4, it takes place between $\alpha \approx 0.56$ and $\alpha \approx 0.88$. This shift may be a consequence of the protection effect that the solubilization layer of CP^+ ions has on the hydrophobic PMA coil. From the titration curves, the standard free energy change, $\Delta G°$, of the conformational transition was calculated. In the case of i-PMA without added surfactant, $\Delta G°$ was obtained form the second titration cycle in order to eliminate the contribution to the free energy change due to the dissolution of i-PMA at low α_N; it was $\Delta G° = 0.3$ RT. In the presence of surfactant, $\Delta G°$ was obtained on the basis of the extended Hendersson-Hasselbalch equation.[2] The values $\Delta G° = 0.71$ and 0.59 RT were obtained for S/P = 0.2 and for S/P = 0.4, respectively, and may contain contributions due to the dissolution of the insoluble i-PMA and to the modification of the compact conformation of i-PMA by the solubilization layer of CPC.

In the second part, binding of CPC to i-PMA at various α_N values was studied by the potentiometric method based on surfactant-selective membrane electrode. Strong interactions between CPC and i-PMA are characterized by low values of the critical association concentration, CAC, which lies between 5×10^{-7} and 5×10^{-6} mol/L. In solutions of i-PMA, CAC is lower than in solutions of a-PMA, which can be ascribed to a more pronounced hydrophobic character of i-PMA. On the other hand, degree of binding at the plateau region of binding, where the polymer chain becomes saturated with surfactant, is somewhat larger in the case of a-PMA. This was interpreted by taking into account the difference in the flexibility of both polymer chains. In some cases (for i-PMA at $\alpha_N < 0.5$, and for a-PMA for $\alpha_N = 0$), two-step binding isotherms were observed.

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The Influence of pH on the Precipitation of Amorphous and Crystalline $CaCO_3$

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Amorphous calcium carbonate (ACC) particles were prepared from aqueous $CaCl_2$-dimethyl carbonate-NaOH systems[1] at ambient temperature, at different pH values ranging from 11 to 13 and with different dimethyl carbonate concentrations. The samples were identified as ACC, calcite and vaterite by means of powder X-Ray diffractometry, scanning electron microscopy, TG-DTA and FT-IR spectroscopy. Adding different amount of dimethyl carbonate to the aqueous solution has no effect on the morphology and size of the particles. At initial values between 11 and 12 the rhombohedral calcite and spherulites vaterite formation is observed. At higher initial pH amorphous calcium carbonate, calcite and vaterite are detected. The degree of cristallinity depends on the nucleation time. The longer the salt remains in solution, the more crystalline will be the resulting precipitate.

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pH and Specific Ion Effects in Buffer, Polyelectrolyte and Protein Solutions - a Comparative Study

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Changes in pH induced by the addition of electrolytes to buffers, polyelectrolytes and to proteins (casein, whey and lysozyme) solutions were explored systematically. The two buffers were triethanolamine / triethanolammonium chloride, and citric acid / sodium citrate. These were chosen because of the similarity of their acid-base equilibria with those of amino acids predominant in most proteins i.e. amino acids that include carboxylate or ammonium groups in their structures. The pH of triethanolamine and of citrate buffers respectively increases and decreases when salt is added. At low electrolyte concentrations (<0.15 mol/kg), the phenomenon can qualitatively be described for by standard electrostatic theories. But strong ion specificity shows up at higher salt concentrations. This specificity follows the usual Hofmeister series for both anions and cations.

The pH of polyelectrolyte and protein solutions with added salts mimicked these observations: (i) From only the primary structure of a polyelectrolyte or a protein it is possible to determine easily the sense of pH variation of a solution containing this protein through salt addition at ionic strengths lower than around 1M. (ii) This similarity shows that the ion specificity of pH changes of buffer solutions has the same origin as the Hofmeister effects observed for pH variations in casein, whey and lysozyme solutions and probably in general protein in solutions.

A novel approach to ion specificity in proteins then emerges. It is based on an understanding of the ion specificity observed in the acid-base equilibria of structural units of proteins. Such a phenomenon may play an important role in regulating enzyme activity.

Simulation of Binary Hard-Sphere Systems at the Colloidal Limit

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The model of hard-sphere binary mixtures plays an important role as reference for simple fluids and colloids.[1] Colloid models usually do not take into account the solvent explicitly. The aim of our studies was to clarify how much this treatment is justifiable. Binary hard-sphere systems have been extensively studied in recent years, but there are only a few studies, where the size ratio of the particles corresponds to the colloid particle/solvent molecule one. Computer simulations can be applied to investigate it exactly, but when the packing fraction of the small spheres becomes substantial the number of the particles reaches the computational limit: at radius ratio q=0.1 a system consisting of 100 big spheres requires 10^5 small spheres, if the packing fractions of both components are to be 0.1. Therefore, a complete set of simulations cannot be found in the literature. These investigations involve mostly approximate theoretical calculations about phase diagrams[2,3] and contact values[4] of the pair-correlation functions, and the simulations are performed with a limited number of big particles, and there is no result to be found about the big-big particle distributions at medium or large packing fractions.[5]

We developed a hard-sphere molecular dynamics code to simulate these asymmetric binary systems. We calculated the partial pair-correlation functions with size ratios q=0.1 and q=0.2. The packing fractions of the components were between 0.1-0.5. The pair-correlation functions show some new features of the systems compared to the previous theoretical results.

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Liquid-Liquid Equilibria of Aqueous Two-Phase Polypropylene Glycol – Sodium Citrate System at Different Temperatures

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Liquid-liquid extraction utilising aqueous two-phase systems has been used to separate and purify biological products from the complex mixtures in which they are produced. In this respect, the phase behavior of these systems are necessary for the design of extraction processes. Polyethylene glycol (PEG), which is a hydrophilic polymer, is often used in aqueous two-phase partitioning studies. Polypropylene glycol (PPG) is a polymer that is structurally closely related to PEG. Low molecular weights of PPG are completely soluble in water while high molecular weights are only partially soluble. This polymer can also be used for the separation of biomolecules, since its aqueous solutions with a suitable polymer or a salt forms a two-phase system. However, liquid-liquid equilibrium (LLE) data of the aqueous PPG–polymer and PPG–salt systems are relatively scarce. In this work Liquid-liquid equilibrium data of the poly ethylene glycol 400 + sodium citrate + water has been measured at (20, 30, 35 and 45) °C. The binodal curves were described using the binodal model and a three-parameter equation. The tie lines were satisfactorily described using the Othmer-Tobias and Bancroft equations.

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Thermodynamic Characteristics of the Mixed Solvent Components Interaction with the Cellulose Material

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The influence of ways of cellulose desintegration on its structural and sorption properties and reaction ability was investigated. The thermodynamic characteristics of water desorption process for the kraft-cellulose subjected by mechanical (on the plant of percussive-reflect principle and on the extruder) and chemical (hydrolysis by nitric acid) disintegration were obtained. It was shown, that the reaction ability of the cellulose correlates with the water maximum sorption value, instead of the total amount of the bounded water in cellulose. The sorption properties of cellulose, and, accordingly, reaction ability are caused not so much by a crystallinity degree, as the reorganization character of the hydrogen bonds as result of the mechanical effect.

The water sorption process on the microcrystalline cellulose is determined by the microporous structure, instead of interaction with the active centers, i.e. hydroxyl groups of cellulose. An inorganic electrolyte (NaCl) addition to the water – cellulose system does not influence essentially on the thermodynamic characteristics of the water desorption.

The thermodynamic characteristics of the mixture components desorption for the cellulose-water-DMSO and cellulose-water-EtOH systems were obtained. The different nature of cellulose interaction with the water-EtOH and water-DMSO mixtures caused by different ability of the mixture components to form hydrogen bonds with the cellulose hydroxyl groups was indicated. The water sorption dominates for the cellulose – water-DMSO system in the DMSO concentration range $0 < x_D < 0,28$, and at the DMSO concentration $x_D \sim 0,1$ the water sorption takes on the maximal value. The hydrogen bonds formation between cellulose hydroxyl groups and DMSO oxygen atoms is the most probable in the DMSO concentration range $x_D > 0,6$ when „big“ clusters formation prevails over formation of dimers having hydrophobic properties. The enthalpy of EtOH desorption in the water-EtOH-cellulose system is equal to zero practically in all over the concentration range.

C.

BIOINORGANIC, BIOPHYSICAL AND PHARMACEUTICAL PROBLEMS

Oral Presentations

Spectroscopic Study of Equilibria Between Aluminium(III) – Ion and L-Histidine in Aqueous Solutions

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Solution equilibria between aluminium(III) ion and l-histidine (HHis) were studied by UV spectrophotometry, ESI-MS, and multinuclear NMR spectroscopy. To evaluate the complexation in histidine + Al^{3+} solutions several series of solutions were prepared. The total concentration of histidine was 250.0, 50.0, 25.0 and 1.0 mmol/dm^3 while that of aluminium was 100.0, 50.0, 12.5, 5.0 and 0.5 mmol/dm^3 in the pH interval 1.8 – 6.4. The prepared solutions were left to stand 72 h before measurements were made. Analysis of the UV spectra of histidine + Al^{3+} solutions in the wavelength interval 240 – 350 nm indicated the formation of two main complexes, $Al(HHis)His^{2+}$ and $Al_2(OH)His^{4+}$. ESI-MS indicates intensive hydrolysis in solutions and confirms formation of the dimmer. At pH 4.06 (Fig. 1) the 27-Al NMR spectrum of the solution with histidine to aluminum, 5:1 molar ratio, in addition to aqua-Al resonance at $\delta \sim 0$ ppm shows the resonances at 4.69 ppm, broad peak at $\delta \sim 9.54$ ppm and sharp resonance at 63 ppm. The resonance at 9.54 ppm is near to expected value of $\delta \sim 10$ ppm when the amino acid acts as bidentate ligand[1] and may be thus, assigned to the formation of binary complex between aluminium ion and histidine. In this pH region the dominating complex is $Al(HHis)His^{2+}$[2] and therefore, protonated histidine acts as a bidentate ligand in fairly symmetrical environment. Bearing in mind that pK_a value of pyridinic nitrogen in imidazole residue is about 6.5 it appears that the proton resides on this donor. Thus the complex is formed by binding carboxylate oxygen and amino group of histidine to aluminium ion.

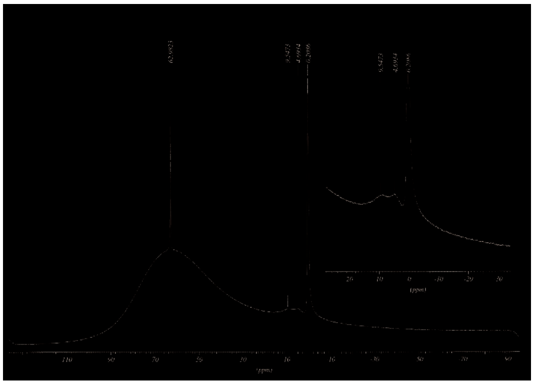

Fig. 1. *^{27}Al-nmr spectra of histidine+Al^{3+} solution (250:50 mmol/dm^3) at pH = 4.06*

The resonance at ~ 4.7 ppm was assigned to the mixed hydrolytic dimmer [Al2(OH)His]4+, while the resonance at 63 ppm belongs to the hydrolytic tridecamer. Proton and 13C NMR spectra indicate involvement of carboxylate and amino group in coordination of histidine to Al. The main complex $[Al(HHis)]HisCl_2$ was synthesized and characterized by elemental analysis and IR spectra.

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Solution Chemistry of Metal Complexes of 2-Furancarboxaldehyde

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Solution chemistry gains momentum in recent years due to its application in the field of biology. 2-Furancarboxaldehyde (fural), a well known natural compound used extensively in the vegetable oil, petroleum, paint and rubber industries, is recently exploited in the cosmetic industry as a skin protecting agent against natural radicals like OH, H, O etc. Hence an interaction study of fural and biologically important metal ions Co(II), Ni(II), Cu(II) and Zn(II) were studied in solution phase through potentiometry and gas phase using ab initio HF/6-31G* and MP2/6-31G* methods. Ground state geometries were optimized and tested through frequency analysis. For simplicity 1:1 species is consider for the present work. It was found that fural is a bidentate ligand and binds through furan oxygen and carbonyl oxygen with the entire four metal ions in gas and solution phases. If the ligand is mono dentate it binds through carbonyl oxygen. The order of binding effect is furan oxygen < carbonyl oxygen. Regarding the structural reactivity relationship the furan oxygen binds the metal ion through s and p_z orbitals. The carbonyl oxygen binds through s and p_y orbitals. The binding effects and modes of both the oxygens are differing. Furla forms high spin complex with Co(II) and Ni(II) with the multiplicity of 4 and 3 respectively. The strength of Cu(II) – fural binding in both gas and solution phases are less than the expected. This is because of the week binding of furan oxygen. The order of binding in solution phase is Co(II) < Ni(II) < Cu(II) > Zn(II). The theoretical stability follows the order Co(II) < Ni(II) < Cu(II) < Zn(II).

Solution Conformation of Insect Hormones by NMR Restrained Molecular Dynamics

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Insects form one of the largest groups of multi-cellular organisms inhabiting our planet. They are widely distributed and generally highly mobile. Important in this regard is their ability to fly. Insect flight metabolism is under hormonal control via the AKH/RPCH (adipokinetic hormones or red concentrating pigment hormones).[1] These hormones regulate the hydrolysis of fat stores of triacylglycerides to diacylglycerides and their subsequent transport to muscle cells. More than 30 different AKH/RPCH hormones have now been isolated Distinguishing features of these hormones include that they are all octa-, nona- or deca-peptides with blocked N- (pyroglutamate) and C-(amidate) termini and that they display a high degree of homology. The hormones are released in the brain and bind to G-coupled protein receptors which initiates the cellular response. We have used nmr techniques to study the solution conformation of the AKH and related peptides.[2,3]

Crustacean cardio-active peptide is a hormone which has been identified in a number of insects. It is a nonapeptide with a disulfide bridge between the two cysteines (3 and 9).

Pro – Phe – Cys – Asn – Ala – Phe - Thr – Gly – Cys – NH_2

This peptide has been studied in DPC micelle solution. Vacuum simulations resulted in an unusual trans/cis isomerisation. A molecular dynamic search of CCAP in a biphasic water/decane solvent box resulted in two clusters as shown in Figure 1. Both clusters showed a β-turn motif which is a motif common to many GPCR binding peptides.

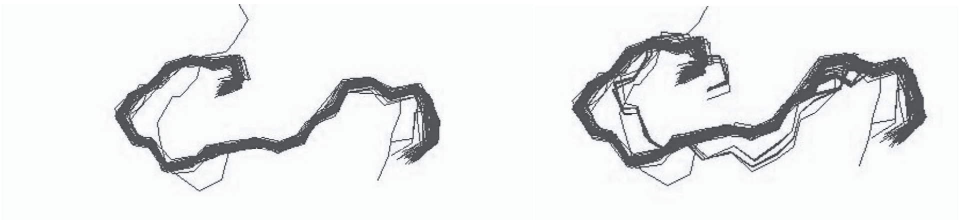

Figure 1. Two predominant clusters found for CCAP in a water/decane solvent box.

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Biologically Relevant Metal-Ion Polyphenol Interactions

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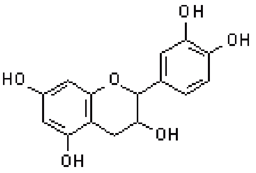
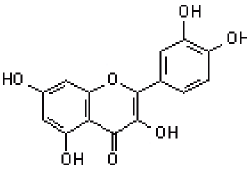
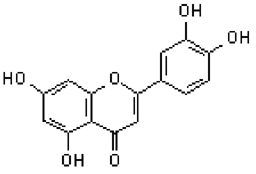
Polyphenols constitute one of the most numerous and ubiquitous groups of plant metabolites and are an integral part of both human and animal diets. They range from simple phenolic molecules to highly polymerised polytopic compounds capable of binding two or more metal ions in different environments. Nowadays, the key role played by polyphenols in the diet is recognised as being due to their antioxidant and metal binding properties. Possible beneficial effects of polyphenols include their role in preventing cancer, cardiovascular disease and other diseases. The general structures of some categories of polyphenols are outlined below.



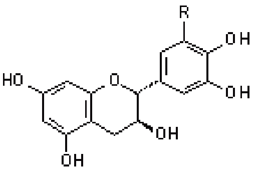
Flavanol



Flavonol



Flavone



R = H; Catechin
R = OH; Gallocatechin

The present investigations have concentrated largely on the reaction of aluminium(III) and iron(III) with polyphenols. Aluminium(III) is redox inert while iron(III) is redox active and in general complexation of iron(III) by polyphenols is followed by an electron transfer reaction in which the iron(III) is reduced to iron(II). The presentation will describe recent results of investigations into the kinetics and mechanisms of these reactions and these will be discussed in terms of previously published work.[1-6] The presentation will concentrate on the reactions of polytopic polyphenols and the structural features which determine whether or not an electron transfer reaction takes place when iron(III) is bound to a polyphenol.

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Thermochemical Investigations of Salting Processes of Hen-Egg White Lysozyme in Various Electrolyte Solutions

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Prediction of the solution conditions where proteins aggregate and successfully crystallise remains a significant obstacle in the advancement of structural molecular biology. Most of the problems arising in protein crystallisation are due to our incomplete understanding of protein-protein interactions. Thermodynamic investigations can provide very useful information about the energetics of the nucleation behaviour.

The results of long-term project of thermodynamic investigations of salting processes of hen-egg white lysozyme in various electrolyte solutions [NaCl, LiCl, KCl, K_2SO_4, Li_2SO_4, $(NH_4)_2SO_4$] are reported. The experiments were performed with the use of a conduction microcalorimeter, ITC Omega MicroCal and LKB batch microcalorimeter.

It was demonstrated, that the kinetics of crystallization of lysozyme salted by NaCl can be determined with the use of conduction microcalorimeter. The process was monitored continuously for more than 10 hours. The obtained calorimetric data are in good agreement with the nucleation behaviour deduced from light scattering (DLS) and NMR experiments. DLS experiments showed a systematic increase of the aggregates size, while upon NMR DOSY experiment in the hour time scale no significant changes of the diffusion coefficient were observed. After ~70h of NMR experiment 2.1 mM lysozyme solution in 0.5 M NaCl solution started to crystallize/aggregate, which was indicated by the decrease of both translational and rotational diffusion coefficients. Analysis of the salt induced changes in 2D-^{1}H TOCSY spectra enabled to determine the ion binding sites on the lysozyme surface. Their location generally agrees with the partial occupancy of iodide anions in lysozyme crystal.

Changes in enthalpy of salting as a function of concentration of electrolytes enables to distinguish two steps of salting process (salting-in and salting-out). It was found that the estimated number of binding sites depends on the lysozyme concentration. In the low salt conditions the estimated number of anion binding sites on the lysozyme surface initially decreases, and remains almost constant, when the concentration of lysozyme exceeds ~2 mM. In the high salt conditions the specific uptake of ~2 chloride anions undergoes at ~0.63 M NaCl concentration.

The enthalpy of salting, according to McMillan and Mayer's approach, has been analyzed in the terms of lysozyme - lysozyme h_{xx}, and lysozyme - salt interaction $h_{xy.}$ Changes in these parameters with an increase in electrolytes' concentration were observed.

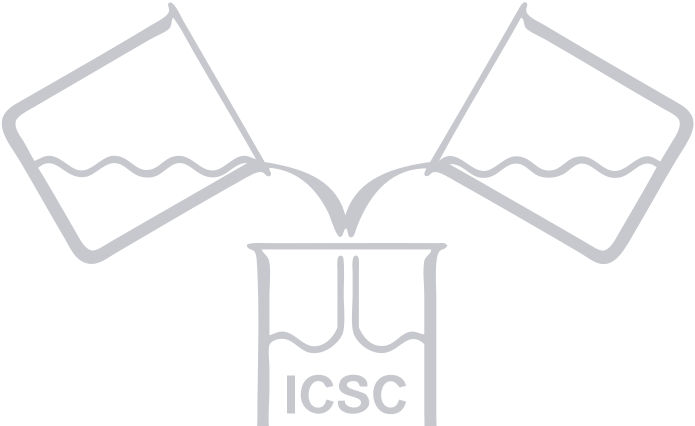
The efficiency of cations in the salting-out process of lysozyme can be seen from the following series : $Li^+ >> Na^+ > K^+ > NH_4^+$.

The apparent molar volumes of solutions studied were determined. The changes of the enthalpy and apparent molar volumes vs. concentration of electrolytes studied have been found to follow similar course . The beginning and end of salting-in process of lysozyme for various electrolytes can be distinguished. The conclusions are in good agreement with Retailleau et al. data on variation of lysozyme solubility vs. NaCl concentration.

C.

BIOINORGANIC, BIOPHYSICAL AND PHARMACEUTICAL PROBLEMS

Poster Presentations



An Ultrasonic Study of Some Drugs in Solutions

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Density, ultrasonic velocity, refractive index and viscosity of loratidine, cetrizine and chlorpheniramine have been studied in methanol, dimethylformamide and dimethylsulfoxide at 308.15 K. From the experimental data, various acoustical parameters have been evaluated which helps in understanding the moleculer interactions occurring in these solutions.

Kinetics of Target Site Localization of a Protein on DNA in Solution: a Stochastic Approach

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It is widely recognized that the cleaving rate of a restriction enzyme on target DNA sequences is several orders-of-magnitude faster than the maximal one calculated from the diffusion-limited theory. It was therefore commonly assumed that the target site interaction of a restriction enzyme with DNA has to occur via two steps: one-dimensional diffusion along a DNA segment, and long-range jumps coming from association-dissociation events. We propose here a stochastic model for this reaction, which comprises a series of one-dimensional diffusions of a restriction enzyme on nonspecific DNA sequences, interrupted by three-dimensional excursions in the solution until the target sequence is reached. This model provides an optimal finding strategy which explains the fast association rate. Modeling the excursions by uncorrelated random jumps, we recover the expression of the mean time required for target site association to occur given by Berg et al. in 1981, and we explicitly give several physical quantities describing the stochastic pathway of the enzyme. For competitive target sites we calculate two quantities: processivity and preference. By comparing these theoretical expressions to recent experimental data obtained for EcoRV-DNA interaction, we quantify: 1), the mean residence time per binding event of EcoRV on DNA for a representative one-dimensional diffusion coefficient; 2), the average lengths of DNA scanned during the one-dimensional diffusion (during one binding event and during the overall process); and 3), the mean time and the mean number of visits needed to go from one target site to the other. Further, we evaluate the dynamics of DNA cleavage with regard to the probability for the restriction enzyme to perform another one-dimensional diffusion on the same DNA substrate following a three-dimensional excursion.[1]

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Synthesis and Chelating Properties of a New Sulfonamide-Hydroxypyrimidinone Chelator

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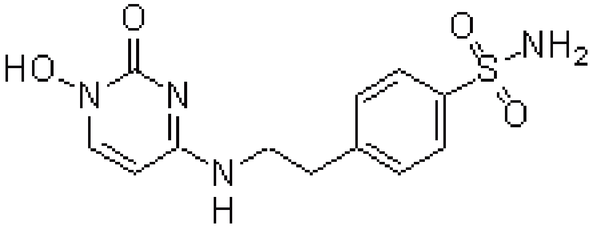
The hydroxypyrimidinones are a kind of endocyclic hydroxamic acids with high affinity for hard metal ions and some recent research has been focused on their potential application as toxic metal decontaminants for environmental and biological/pharmacological purposes.[1] Moreover, the hydroxamate group is the preferred metal-binding group for the inhibition of zinc-containing enzymes, such as the matrix metalloproteinases (MMPs), which are involved in several processes associated to matrix degradation, namely the tumor cell invasion and joint destruction in arthritic conditions.[2] On the other hand, the sulfonamides are known as good inhibitors of other zinc-containing enzymes, such as the Carbonic Anhydrases (CAs), associated to important physiological and pathological situations.[3] Therefore, a new hydroxypyrimidinone compound incorporating a sulfonamide moiety was prepared and studied aimed at potential improvement of enzymatic inhibition activity.



(I)

Herein, we present the solution equilibrium studies of 4-[2-(4-sulfamoyl-phenyl)-ethylamino]-1-hydroxy-2(1*H*)-pyrimidinone **(I)**, namely its acid-base properties and its complexation behaviour towards Zn(II), involving potentiometric and spectroscopic techniques. The set of results obtained for this bifunctional derivative allows the identification of the preferred zinc binding modes. Discussion of the present results is mostly based on comparison with those of parent mono-functional analogous (hydroxypyrimidinone, sulfonamide). Bioassays are under way to evaluate the enzyme inhibitory activity.

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Proteins in Aqueous Two-Phase Systems

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Characterisation of aqueous solutions containing poly(ethylene glycol), dextran and test biomolecules (BSA, lysozyme) by means of membrane osmometry is performed in order to tune the experimental procedure and apparatus and to contribute to the data base of osmotic pressure data prior further investigation on proteins of industrial importance. The osmometric data show dependence of both the number average molecular weight and the osmotic virial coefficient of proteins on pH at relatively low salt (buffer) concentrations. The coefficients obtained are compared with the literature data.[1-4] The large protein molecular weights obtained indicate that monomers self-associate to form dimers and higher oligomers under the conditions employed and the observations are in fair agreement with the literature.[5] Some partitioning data are reported for test biomolecule BSA and lysozyme at different pH, including the phase composition and densities of the both phases. The calculation procedure for estimating partitioning of proteins at conditions slightly different from experimental ones is outlined.

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Calculation of Heat Capacity of Protein by Using Extended Scaled Particle Theory

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Heat capacities of two proteins, avian pancreatic polypeptide (PPT) and bovine pancreatic trypsin inhibitor (BPTI), are calculated by using extended scaled particle theory (XSPT) which has been developed by us.[1] Thermodynamic quantities relating to a solvation process of a solute are derived in XSPT based on statistical mechanics. A solute molecule is treated at atomic level. Energy and structure parameters used in molecular dynamics of protein are adopted.[2] Effect of conformational difference can be taken account in the theory. Calorimetry experimentalists often assume that heat capacities of protein are dominated by hydration effect of proteins. In this study, temperature dependence of hydration free energy is used to calculate the heat capacities of proteins. We used two state model. Native and denatured conformations are an X-ray crystallographic conformation and a computer generated conformation, respectively. Candidates of denatured conformations in this study are two extended conformations (fully extended, "extended 1", and all beta-strand ,"extended 2") and three random conformations ("random 1, 2, and 3"). A polypeptide consisting of 36 residues, PPT, contains one alpha helix and has cylinder shape. A small globular protein consisting of 58 residues, BPTI, contains one alpha helix and one beta sheet composed of two beta strands. Calculated heat capacities show that proteins have constant values in the range of 273-373 K, which is known in calorimetric experiments of proteins. Experimental values at native states are in the same order of the calculated ones. Experimental values at denatured state fall in between the calculated results at native and denatured states.

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Copper(II) as a Potential Factor in Adverse Effects Related to Antibiotics Metabolism

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Copper is one of the most essential trace elements for biological processes. It serves as a cofactor, as well as prostetic group for several enzymes. Moreover Cu^{2+} ions also influence specific gene expression. The major copper-transporting systems in blood plasma include ceruloplasmin, albumin, and transcuprein, but it is also bound to a variety of low molecular weight ligands. Normal concentration of this metal in blood serum amounts to 18 ± 2 μM.[1] It is not controlled there as tightly as inside the cell, and is often elevated in some pathological conditions, including cancer, inflammation, hyperthyroidism or some neurodegenerative diseases. In unbound form, copper can generate hydroxyl radicals and thus mediate DNA damage, proteins oxidation or plasma lipids peroxidation. Xenobiotics, e.g. antibiotics, are likely to participate in such processes by binding Cu^{2+} ions and modulating its oxidative properties.

We have studied a wide range of antibiotics with respect to their coordination properties towards Cu^{2+} ion. Tetracyclines,[2] lincosamides[3] and especially aminoglycosides[4-6] form at physiological pH stable complexes with this metal. The resulting species possess very interesting oxidative features by generating hydroxyl radicals, as well as DNA and RNA damage. The RNA cleavage was proved to proceed at the abasic site, what is of the significant importance for toxicology of aminoglycosides.[7]

Actinomycin D, a cytostatic chromopeptide antibiotic, which is known to interrupt copper homeostasis, proved the tendency to bind Cu^{2+} and its cleaving potency towards DNA was the highest when compared to other antibiotics.[8] Also sinefungin, the antiviral and antifungal agent, which molecule combines the elements of adenosine and ornithin seems to gain an aggressive behavior by binding Cu^{2+} ion. The oxidative reactions, which proceed in the presence of the complex are much enhanced than for uncomplexed metal. They could be even intensified, when accompanied by physiologically ubiquitous substances or antioxidants.

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Transition Metal Complexes of Peptide Fragments of Prion Protein Outside the Octarepeat Region

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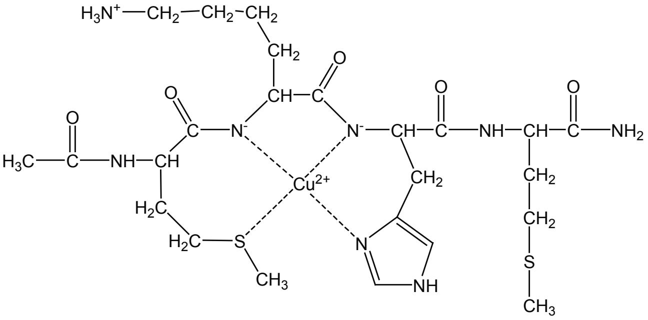
Conformational changes of prion protein (PrP) are responsible for a series of neurodegenerative disorders such as mad cow or Creutzfeldt-Jakob disease. Although the normal function of these proteins is still unknown, it is thought that these proteins play an important role in copper metabolism. Now it is well demonstrated that prion protein can bind copper(II) with high selectivity. It also has been suggested that transition metal ions also can stabilize or modify the secondary structure of this protein.

In this study we report the results of combined pH-potentiometric, UV-VIS, CD, NMR and EPR spectroscopic studies of four different regions of HuPrP (109-112 tetra-, 106-114 nona-, 94-97 tetra- and 184-188 pentapeptides) and some ChPrP analogues (122-125 tetra- and 119-127 nonapeptides) with Cu(II), Zn(II), Ni(II), Cd(II) and Pd(II) metal ions. It was found, that all of these segments have higher affinity for copper(II) binding compared to the octarepeat region, and the other donor sites – besides the imidazole nitrogen – can have a significant effect on the complexation processes. For example the complex with [$CuH_{-2}LH$] stoichiometry can be characterised by an (N(im), N^-(amide), N^-(amide), S(thioether)) (see Figure) coordination mode in case of HuPrP(106-114) and HuPrP(109-112), while the (N(im), N^-(amide), N^-(amide)) coordination is characteristic of the other peptides.

On the other hand the metal binding affinity can be described by the following order: Pd(II) > Cu(II) > Ni(II) >> Zn(II) ~ Cd(II). The highest thermodynamic stability and selectivity were observed in case of Pd(II) where the coordination starts at very low pH value by the binding of thioether residue, but under physiological conditions the nitrogen atoms (N(im), N^-(amide)) are the main binding sites. Deprotonation and coordination of amide group can also be seen in case of Cu(II) and Ni(II) in basic solutions, but only a low stability constants could be calculated for Zn(II) and Cd(II) complexes.



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Thermal Stability of DNA in Aqueous Solutions of Diethylsulfoxide

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Diethylsulphoxide (DESO) has unusual physicochemical properties, and like DMSO exhibits biomedical significance.[1,2] In this communication we present new results on the influence of DESO on the thermal denaturation of calf-thymus DNA studied by two methods: UV absorption and vibrating-tube densimetry. To elucidate the effect of DESO on the thermal denaturation of DNA the obtained results were compared with those for DMSO.

In all cases, melting temperature (T_m) decreases with an increase of sulfoxides concentration and the decrease becomes much more pronounced at higher concentrations of sulfoxides. The values of dielectric constants (ε_s) at temperature ranges from 293 to 333 K are changing from 46.6 to 43.0 for pure DMSO and from 44.1 to 39.4 for pure DESO.[3] Thus one can conclude that solvent polarity actually could not be considered as a crucial factor of its influence on the DNA melting when DMSO and DESO were used.

It should be noted that the results obtained will be useful for revealing the role of hydrophobic interactions in proteins and in the structural stability of DNA in aqueous solutions of non-electrolytes. In this respect it is worth noting to consider the possibility of a direct interaction of DESO with DNA similar those, which take place between lipid and DESO.[4] On the other hand, the stability of DNA is not only determined by its direct interactions with solute (sulfoxides) molecules. Another very important factor is the structural change of the whole aqueous solution, partly due to the insertion of the nonpolar ethyl groups of DESO into intercluster space of water and leading to the setting of hydrophobic interaction.[5]

An explanation taking into account the structural peculiarities of DESO+ water system[5,6] has been presented.

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Acid-Base Properties of Flavonoids in Ethanol-Water Solvent Mixture

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Although a number of publication have been made on the analytical uses of flavonoids,[1,2] neither the effects of the water and alkaline buffers (e.g. phosphate at pH ≈ 7.4-7.5) nor the content of various ionic strengths satisfactorily have not been elucidated on the properties and coordination of flavonoids. Only a few papers have dealt with the effects of medium considering alternative possibility of oxidation and complexation.[3] Our study on acid-base properties of three flavonoids, quercetin, rutin and robinetin, was the first part of investigation of their chelating with Aluminium(III) and Copper(II).

The protonation constants of quercetin and rutin were determined in 50:50 v/v ratio of ethanol and water mixture, which solvent could be either proton acceptor or proton donor, and had less oxidative feature for testing of flavonoid metal interactions, by potentiometric - spectrophotometric measurements. On the evidence of the absorption spectra plotted against pH of the solutions it has been realized that quercetin seems to be a monoprotic acid (pK = 6.93) in contrast to rutin, which dissociates in two steps (pK_1 = 6.73; pK_2 = 8.73). Both computer program and graphic representation were used for determination of the dissociation constants of these flavonoids and the numerical values are only slightly different from the data of bibliographies[4,5] in consequence of the different composition of solvents. Nevertheless there were some references with significant difference in the value of dissociation constants of quercetin,[6,7] but the procedures of these researches were not absolutely right.

The more speedy irreversible structural transformation of quercetin and robinetin the higher pH were detected from their UV-VIS spectral changes by the time and these changes were appeared immediately after the dissociation processes even though in a weak basic solution. The apparent rate constant of the irreversible transformation of quercetin was determined, too. The reaction steps included the processes of dissociation, tautomer and mezomer transformations, respectively, and the water addition at the end. Even if different reaction steps of structural changes were recognized in strong alkaline and weak basic solutions, the products had the same protonated forms. On the other hand only dissociation equilibrium of rutin could be observed in the same conditions.

Our spectrophotometric results flashed a light on the contradiction perceived in potenciometric measurements of these flavonoids, above all in the case of quercetin, in addition the differences of dissociation constants also could be explained. The results of investigation of spectra depending on pH supported that the chelating is worth examining in only acidic or neutral media without irreversible change of quercetin and hydrolysis of metal ions. The series of flavonoid spectra, determination of dissociation constants and the schema of structural transformation will be displayed on the poster presentation.

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Metal Binding Strengths of Peptide Hydroxamic Acids

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The biological activity of hydroxamates is well known. Some results have also been published on the inhibition of hydroxamic acid derivatives of amino acids and peptides on metalloproteinases. Compared to the simple hydroxamic acids the presence of the amino groups and the peptide chain may increase the number of coordination modes.

In the present work the complexes of Fe(III), Al(III), Zn(II), Cu(II) and Ni(II) with AlaAlaNHOH and AlaSerNHOH and their protected derivatives (Z-AlaAlaNHOH and Z-AlaSerNHOH) have been studied. Ligands were synthetized from protected dipeptide methyl esters and hydroxylamine in dry methanol. The protecting group was removed with H_2 in the presence of Pd/C in methanol. The structure and the purity of the compounds were checked and determined by TLC, NMR and potentiometric titrations. In order to determine the stoichiometry and stability constants of the metal complexes formed in aqueous solutions pH-potentiometric and different spectroscopic techniques (UV-Vis, NMR, EPR) were used.

While the protected derivatives have only one (HA), the unprotected derivatives have two dissociable protons (H_2A^+). Because in the latter case the dissociation processes overlap we have also calculated the dissociation microconstants of the ligands.

With the „hard" Fe(III) the hydroxamate oxygen donors can be coordinated for all the four ligands below pH=2. At ligand excess and at higher pH the formation of 1:2 and 1:3 complexes and mixed hydroxo complexes were also detected. The stability data for these species show that the protected derivatives form more stable complexes with iron(III).

In the Al(III) systems the coordination of the hydroxamate group was also detected. With increasing pH, however, the hydrolysis of the metal ion is found to be more significant.

With Zn(II) again the involvement of the hydroxamate group of the protected ligands was detected, while for the unprotected ligand systems both (O,O) and (NH_2, O) coordination takes place.

For the „nitrogenphilic" Cu(II) and Ni(II) the coordination of the amino group and the peptide chain occurs. With Ni(II) the complex formation starts at higher pH and only on nitrogen donor groups, with the formation of square-planar complexes. In Cu(II) systems the complex formation starts at pH ~ 4.0 on hydroxamate oxygen donor groups. On increasing pH the coordination mode changes and the nitrogens are coordinated to the metal center. Multinuclear species were also detected and their nuclearity and solution composition was proved by UV-Vis and EPR measurements.

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An EPR Spectroscopic Study of Copper(II) Complexes of L-Phe – Cis-2-Amino-Cyclohexanecarboxilic Acid Diastereomers

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Because of the natural occurrence and biological activity, interest in chemical investigations of the alicyclic β-amino acids has rapidly increased. In spite of the fact, that the metal ions - in particular copper(II) - could have substantial impact on biologic properties, up till now no efforts have been made to clarify the complexation abilities of alicyclic β-amino acids and their peptide derivatives, or to determine the structures of their metal complexes.

Accordingly, we aimed to study the coordination properties of a series of α-amino acid - alicyclic β-amino acid dipeptides e.g. L-Phe-cis-2-aminocyclohexanecarboxilic acid to copper(II) by EPR spectroscopic method. Diastereomer formation was observed in the dipeptide syntheses since the 2-aminocycloalkilcarboxilic acids have enantiomer structures. In the first stage of investigations the racem ligands were examined in order to clarify if this technique could differentiate the coordination abilities of diastereomers.

If we want to obtain the individual spectra of alternative complexes from the experimental curves, we have to decompose the superimposed spectra. We applied for this purpose the two-dimensional EPR simulation, which involves the simultaneous analysis of series of EPR spectra recorded at various concentrations and pH values. It gives the formation constants of the metal complexes including isomers; furthermore, it furnishes the magnetic parameters of the EPR-active species, which offer information about the nature of coordinating groups and coordination modes.

The protonation constants of the free ligand were determined by pH-potentiometric method. EPR spectra were recorded at 1:1, 1:5 and 1:15 copper(II) to ligand concentration ratio. The number of the independent EPR-active species was determined by matrix rank analysis of the spectra; altogether five species were found. Experimental curves were fitted by 2d_epr program[1]; the best fit was obtained when the equilibrium model included the species: Cu^{2+} (aqua complex), $[CuL]^+$, $[CuLH_{-1}]$, $[CuLH_{-2}]^-$ and $[CuL_2H_{-1}]^-$. Furthermore a little quantity of $[CuLH]^{2+}$ should also be included to obtain satisfactory fit in the low pH range. EPR-inactive complex $[Cu_2L_2H_{-3}]^-$ (invisible for matrix rank analysis) also have to be included in order to achieve good agreement between the metal ion concentration derived from the spectral intensities and from the analytical concentration data. Moreover, isomer pairs for $[CuLH_{-1}]$ and $[CuLH_{-2}]^-$ complexes were found, which indicates that the complexing diastereomers have indeed significantly different EPR spectra, that is the isomers can be distinguished by EPR spectroscopy. We successfully separated ligand diastereomers by HPLC-technique and we intend their separate investigation in the near future, which could offer the individual set of EPR parameters for the complexing diastereomers, and can help to elucidate the structure-parameter relationship.

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Protonation and Coordination Macro- and Microscopic Equilibria in the Copper(II) – Human Prion Protein (84-114) System

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Conformational changes of Human Prion Protein (HuPrP) are responsible for a series of neurodegenerative disorders such as mad cow or Creutzfeldt-Jakob disease. Although the normal function of these proteins is still unknown, it is thought that these proteins play an important role in copper metabolism. It has also been suggested that transition metal ions can stabilize or modify the secondary structure of the protein.

The segment HuPrP(84-114) is a highly fibrillogenic part of the protein containing the "octarepeat" and the "toxic" part of the peptide, and the amino acid sequence is different in HuPrP and ChPrP. In this study, we report the results of combined pH-potentiometric, UV-VIS, CD, NMR, ESI-MS and EPR spectroscopic measurements on the peptide fragment HuPrP(84-114) and its copper(II) complexes.

^{1}H and two-dimensional NMR measurements (COSY, TOCSY, NOESY and DOSY) show that the conformation of HuPrP(84-114) is unstructured and the deprotonation processes of the three histidines and four lysines occur independently. The deprotonation macroscopic and microscopic constants have been determined.

We found that this peptide containing three histidines is a very efficient copper(II) binder, coordinating at least three copper(II) ions in the neutral and alkaline pH range. The coordination starts with 1N His coordination, and the cooperative deprotonation of two amide nitrogens occurs at neutral pH. In the His96 and His111 position (i.e. in the "toxic prion segment"), the amide deprotonation takes place toward the N-terminus. In the His85 position ("octarepeat region"), however, this process starts toward the C-terminus because Pro84 acts as a breaking point preventing the formation of a 6-membered chelate ring toward the N-terminus. The formation of 4N-coordinated complexes was suggested in alkaline solutions. The same coordination modes were found in the systems containing copper(II) and tetra- and nonapeptides with a single His. In the case of HuPrP(84-114) and at 1:1 and 2:1 copper(II) to ligand ratios, however, the formation of a macrochelate is also possible, increasing the stability of mono- and dinuclear copper(II) complexes. The formation of multinuclear complexes, and the position and coordination mode of copper(II) was studied by ESI-MS and CD spectroscopic methods, respectively. These measurements show that there is no cooperativity in the copper(II) coordination, in spite of the formation of a high amount of binuclear complexes at 1:1 and trinuclear complexes at 2:1 copper(II) to ligand ratios: the high presence of multinuclear complexes can be explained by the statistical distribution weighted with the stability values of the individual His containing fragments. The copper(II) binding ability outside the octarepeat region is stronger than inside. At neutral pH, the stability order is His96 > His111 > His85, in agreement with the results obtained in the systems containing copper(II) and the smaller tetra- or nonapeptide fragments.

Acknowledgement. The Hungarian Research Fund (OTKA D048488 and T048352) is acknowledged for financial support. The present work has also been made possible thanks to the Hungarian (MTA) and Italian (CNR) bilateral agreement.

Study of Conjugate Formation Equilibria of Free Base Porphyrins or Cu(II) Porphyrins with Concanavalin A

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The interactions of several free base porphyrins and their corresponding copper(II) complexes with lectin (concanavalin A) have been investigated by spectroscopic techniques. Experiments have been carried out in water solution and in monolithic silica gels. Porphyrin-protein systems immobilized in monolithic silica gels (obtained by polycondensation of tetraethoxysilane using sol-gel technique) have been also examined by atomic force microscopy (AFM). The present work was concerned on two water-soluble cationic porphyrins: tetrakis [4-(trimethylammonio)phenyl] porphyrin (H_2TTMePP), tetrakis (1-methyl-4-pyridyl) porphyrin (H_2TMePyP), their complexes with Cu(II) (CuTTMePP, CuTMePyP) and two water-soluble anionic porphyrins: tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP) and tetrakis (4-sulfonatophenyl) porphyrin (H_2TPPS).

Studies of lectin-porphyrin interactions can be important from the point of view of the influence of lectins on porphyrin-containing biomolecules and the possible application of these conjugates in photodynamic therapy of cancer (PDT). PDT has attracted a great deal of attention in recent years as a new cancer treatment that utilizes porphyrins and metalloporphyrins as sensitizers. Porphyrins preferentially accumulate in tumour cells, when irradiated by light of appropriate wavelenght, they go into the excited state and cause irreparable damage of cancer cells. Concanavalin A, lectin of the jack bean (Canavalia ensiformis), was found in high concentration in growing tissues and have ability to interact preferentially with transformed (tumour) cells. Due to these properties this protein can be considered as a potential carrier for 3rd generation photosensitizers to tumour tissues.

Porphyrins have another potential application, they could be used as the peptide receptors which work in protic solvents. The goal of selective peptide complexation in aqueous solution was approached only recently, and still needs considerable progress until artificial receptors come close to the efficiency of biological systems.

Both anionic and cationic porphyrins were found to interact with the lectin with comparable affinity, clearly indicating that the charge on the porphyrin does not play any role in the binding process and that most likely the interaction is mediated by hydrophobic forces. Upon binding to concanavalin A an increase in porphyrins fluorescence intensity and a red-shift in absorption and emission maxima have been observed. Each lectin subunit was found to bind one porphyrin molecule. The association constants estimated from absorption titrations for different porphyrins were comparable and were in the range $1 \times 10^4 – 7.4 \times 10^6$ M^{-1} at room temperature. The UV-Vis titrations were carried out in the solution of TRIS buffer with different values of pH (2.8, 8.7 and 10). The strength of association increases with increasing pH and that observation could be explained by various degree of porphyrin protonation and by the conformation of concanavalin A, also depending on pH. Concanavalin A is a multimeric lectin, consisting of non-covalently associated two (below pH 6) or more (above pH 7) the same subunits.

Furfuraldenevalinate: Solution Chemistry of Denticity Reduction, Gas and Solid Phase Complexing Behaviour

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Denticity reduction is the modern aspect of chemistry. It is extensively used for the understanding of natural process. It is believed that origin of species through the combing of biomolecules in water and which is mediated through metal ions. In order to understand this kind of process the present work is aimed to study the Schiff base condensation of 2-furancarboxaldehyde (fural) and L-valine in the presence of Co(II), Ni(II), Cu(II) and Zn(II) ions. It is well documented that fural, L-valine and the above metal ions are highly useful. From the results of the solution study the fural a bidentate ligand present in the metal coordination sphere interacts with the incoming bidentate ligand L-valinate and formed a tridentate Schiff base furfuraldenevalinate of denticity three. This reduction in the denticity is due to entropy effect leads to the fusion of two independent rings. The Schiff base species identified are MAB, M(AB)B and $M(AB)_2$ [AB- Schiff base;
A- fural ; B- L-valine ; M - Co(II), Ni(II), and Zn(II)]. Cu(II) forms only MAB. The Schiff base species are formed around the neutral pH. The gas phase studies were carried out through ab initio HF/6-31G* and MP2/6-31G* methods. Ground state geometries were optimized and tested through frequency analysis. The ligand furfuraldenevaline is a tridentate ligand through furan and carboxylato oxygens and imino nitrogen. The binding ability are carboxylato oxygens > imino nitrogen > furan oxygen. Regarding the structural reactivity relationship the binding effects and modes of both the oxygens and nitrogen are differing. The order of binding in solution phase is Co(II) < Ni(II) < Cu(II) > Zn(II). The solid state studies are also conform the above results.

Molecular Interactions of 1,4-Dihydropyridine Derivatives in Selected Organic Solvents

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Using a combination of volumetric investigations and FTIR spectroscopy, solute-solvent interactions have been investigated for four 1,4 dihydropyridines (1,4 DHP) in selected organic solvents. Apparent molar volumes V_ϕ for nifedipine, nitredipine, nimodipine and amlodipine besilate in acetone, ethanol, DMSO and dichloromethane were experimentally determined using a vibrating tube densimeter. Experimental values for partial molar volume were compared with the calculated volumes from Traube's additivity principle[1] and those obtained by the help of ACD/ChemSketch programme. IR spectra provide an effective mean in investigating intermolecular interactions, especially H-bonded interactions in nonaqueous solution.[2,3] The frequencies of carbonyl stretching vibrations ν(C=O) of 1,4 DHP were correlated with the solvent acceptor number (AN)[3] and discussed in terms of values of partial molar volumes.

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Use of Inverse Gas Chromatography for Determination of Powder Surface Properties

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It is well established that different solid forms (crystal, amorphous) of drug exist, and can influence pharmaceutical drug products differently with respect to processing, stability, dissolution and bioavailability.[1]

Pharmaceutical powders are often isolated from solutions with various procedures that influence their morphology and physico-chemical properties. In order to reduce the size of the particles afterwards the process of milling is often used.

While the isolation methods influence the bulk properties of the powder, milling causes changes only on the surface of the powder particles, but its properties are very important. This can change the dissolution rate of the sample, which is especially important in the case of materials with low solubility in order to increase the bioavailability.

Since the changed surface usually represents very small mass portion of the material (only few percent of the total mass) these changes are difficult to detect with conventional analytical methods (Differential Scanning Calorimetry – DSC, X-Ray Powder diffractometry – XRPD, FT Raman spectroscopy).

Inverse gas chromatography (IGC) is a rather new technique with high sensitivity.[2] It can be used for differentiation between polymorphs, for quantification of amorphous content on the sample surface.

In this research different lactose and indomethacine samples were produced and its surface has been characterised with IGC, Scanning Electron Microscopy, DSC and XRPD.

It has been shown, that inverse gas chromatography can be successfully used for detecting the differences among surfaces of samples and for the quantification of low mass content of the sample amorphous fraction.

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Catalytic Effect of Furfural and Zn(II) Ion in Aqueous Solution

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Proton transfer is one of the simplest and most fundamental reactions in chemistry and is important in oxidation-reduction reactions in many chemical and biological reactions. Since most of proton transfer occurs in aqueous solution, one must consider the role of water molecule in the proton transfer. Water can act not only as a solvent but also as a mediator which gives or accepts proton to promote the proton transfer. Enzymes employ metal ion in several ways. A metal ion can activate a chemical bond and make it more amenable to reaction. Nature has commonly used transition metal ions for such a purpose. Proton transfer from water to carbonyl group is an intermediate for many chemical reactions. It was observed that the direct proton transfer from water to carbonyl is difficult. The water molecule bind with the metal ion felicitates its proton transfer. The present work aims to study theoretically the effect of Zn(II) ion and furfural on the acidity of metal ion bound water molecule. Studies were carried out in gas phase. HF method was employed. 6-31G* basis set was used.

Stable Fragments of the β-Hairpin of Protein G

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We perform all-atom computer simulations on short peptide fragments of proteins, and look for stable states. So far, our tests are on the 14-mer C-terminal β-hairpin of protein G. We use Amber 7, with the parm96 force-field and the generalized-Born solvent model in conjunction with replica-exchange molecular dynamics for 5-7 ns to ensure good Boltzmann sampling. We‘re interested in what chain lengths of the fragments have stable conformations resembling those in the native protein. We find that as the fragment approaches 11 monomer units, the structures begin to converge to a native-like structure. We find that a useful diagnostic for determining whether there‘s a single structure and whether it has converged is to compute the entropy, $\Sigma\, p_i \ln p_i$. We also calculate the free-energy of each state. A large gap in the ground-state free-energy, and a low entropy indicate convergence to a single preferred peptide conformation.

Solution Equilibria of Copper(II) Complexes of Ligands Containing Aspartic Acid

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The carboxylate group is an important binding site of metalloenzymes. The role of the side chain carboxylate group on the metal ion coordination of peptides and peptide derivatives has been widely studied. The data indicate that the effect of the carboxylate groups on the complex formation processes depends on the location of the aspartyl residue in the peptide chain and/or the presence of other donor groups in the ligands.

We have studied copper(II) complexes of two types of aspartic and glutamic acid containing ligands:
(i) di-, tri- and tetrapeptides containing two or more aspartic and/or glutamic acids
(ii) aspartic- and glutamic acid derivatives containing the chelating bis(imidazol-2-yl) residues

The negative charge of complexes of more carboxylate group containing peptides increases, but its effect is almost negligible on the complex formation processes. The side chain carboxylate groups of aspartic acid residues take part in the coordination of copper(II) ions forming a six memebered chelate ring (aspartic acid is at the N-termini) or five and six membered fused chelate rings (aspartic acid is in internal position). These binding modes generally slightly hinder the deprotonation and coordination of the succeeding peptide nitrogens.

In the case of amino acid derivatives containing bis(imidazol-2-yl) group the two imidazole rings are the main binding site forming a stable six membered chelate ring in acidic media. The presence of aspartic acid on the N-termini of the ligand, however, results in the formation of dinuclear species with ligand bridging. The deprotonation and coordination of amide nitrogen takes place in alkali solution, and the weak axial coordination of the side chain carboxylate group promotes the deprotonation of N(1)H group of imidazole ring. It results in the formation of a trinuclear complex via negatively charged imidazolato bridges.

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Real Time Flow Microcalorimetric Study of the Antibacterial Activity of Anionic Surfactants (Sodium n-Alkylsulfates) on the Respiration of *Chromobacterium violaceum*

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Large amounts of Chromobacterium violaceum a Gram-negative rod-shaped bacterium are found in soils and waters of tropical and subtropical areas. In Brazil, significant amount of this microorganism is found in the Negro river, one of the largest afluents of the Amazon river. Following our previous work and experience on biological microcalorimetry,[1,2] in the present work we studied in real time the inhibition effect of a homologous series of surfactants, sodium n-alkylsulfates $C_6 – C_{10}$ and sodium dodecylsulfate (SDS) on the C. violaceum respiration process by using continuous flow microcalorimetry. The respiration heat output production in the presence of each compound was compared with the respiration process in the absence of the bioactive compound. Calorimetric response (CR) for all tested compound at different concentrations allowed us to determine the inhibition concentration of each compound. CR is directly related with the biological activity of the respective compound and showed a linear behaviour with the increase of the number of methylene groups on the compound molecule.

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Replica-Exchange MD Calculation of a Model Peptide in Water and in Ethanol

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Alcohol induced denaturation of peptides and proteins that enhances the α-helical structure has widely been used in protein technology.[1] Although solvent effects on denaturation of proteins have often been discussed in terms of electrostatic interaction by treating medium as a dielectric continuum in biophysics and biochemistry fields, the underlying mechanism has not yet been clarified at the microscopic level.[2]

In the present study, a replica-exchange molecular dynamics (REMD) simulation,[3] one of the generalized-ensemble algorithms, was performed for the first time with a 10-residue model peptide in water and in ethanol that were treated explicitly in order to compare solvent effects on the peptide conformations.

A model peptide of 10 residues was the α-helix fragment of a 28-residues peptide (PDB=1FSD) with a β-β-α motive whose 3D structure had been determined by 2D NMR.[4] The amino-acid sequence is GLU$^-$-LEU-ARG$^+$-ASP$^-$-PHE-ILE-GLU$^-$-LYS$^+$-PHE-LYS$^+$. REMD was incorporated in the MD package program DL_POLY.[5] Replicas at 32 temperatures from 298 to 600 K were used for the REMD simulations. After an equilibration canonical MD run at each temperature for 10 ps, a production REMD simulation of 10^6 time steps (1.0 ns) for each replica was finally performed. Replica exchange was tried every 100 MD steps (0.1 ps).

The radii of gyration (R_g) of the model peptide at the 32 temperatures were calculated in water and in ethanol. The R_g values in water are larger than those in ethanol at all the temperatures. The result indicates that the peptide tends to take more compact structure in ethanol than in water. The numbers of turn structure and intramolecular hydrogen bonds within the peptide were also calculated in water and in ethanol. Both numbers are larger in ethanol than in water. These findings suggest that the intramolecular hydrogen bonds in the peptide are dominant in forming the structure of the peptide in ethanol, compared with those in water. Under this condition, the hydrophilic groups of the peptide tend to combine with each other, resulting in a compact structure via the intramolecular hydrogen bonds.

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Calorimetric and Volumetric Data of Nucleating Bovine Albumin and Albumin From Human Serum at Various NaCl Concentration

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Heat effects and densities of bovine albumin and albumin from human serum in Na – acetate buffer pH 4.2 at various NaCl concentration were determined by LKB 10700-2 microcalorimeter and an Anton Paar 60/602 densimeter (25°C). The density measurement were made after 1, 24 and 48 hours of the dissolution of albumin in the buffer. The correlations between the changes of the enthalpy of salting and apparent molar volumes vs. concentration of salt were determined (Figure).

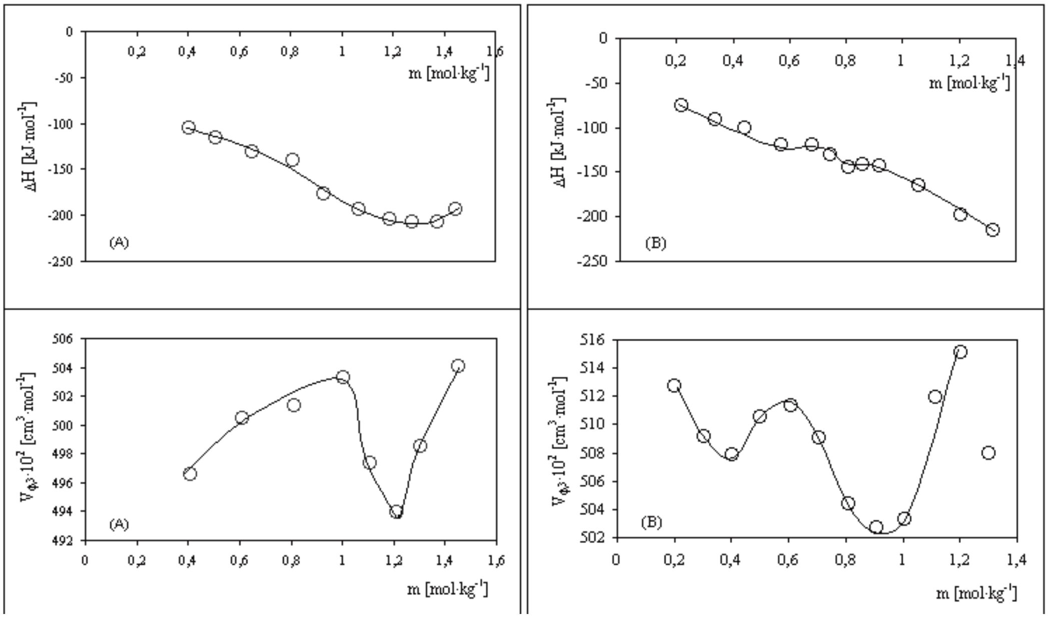

Fig. Comparision of the enthalpy of salting and apparent molar volume (after 1 h) of nucleating bovine albumin (A) and albumin from human serum (B) at various NaCl concentration.

Human Serum Albumin (HSA) Mimicking Ligands as Anti-Inflammatory Agents: Copper and Rheumatoid Arthritis (Ra)

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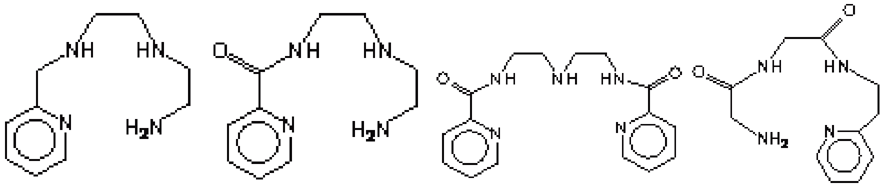
Copper is a biologically essential metal, and has been linked to rheumatoid arthritis (R.A) for centuries.[1] The anti-inflammatory activity of copper complexes has been widely reviewed[2,3] and copper has been observed to possess some potency against inflammation due to RA. The possible use of copper in chemotherapy is reported. Four HSA mimicking ligands (Fig 1) have been synthesized, and their formation constants with biologically important metal ions investigated potentiometrically at 25 ^{0}C and 0.15 M ionic strength. Plasma mobilization indices were calculated using a blood-plasma model[4] while spectroscopic studies were used to determine the structures of the [CuLH$_{-n}$] complex species in solution. Water/octanol partition coefficients were measured and used to estimate dermal absorption of the species. Biodistribution studies were conducted in mice so as to evaluate the drug uptake and retention as well as the in vivo stability.



[555-N] (L^1) [H(555)-N] (L^2) [H$_2$(5555)-N] (L^3) [H$_2$(556)-N] (L^4)

Fig. : Ligands studied

The results of these studies will be presented. They demonstrate the feasibility of using copper complexes as anti inflammatory agents.

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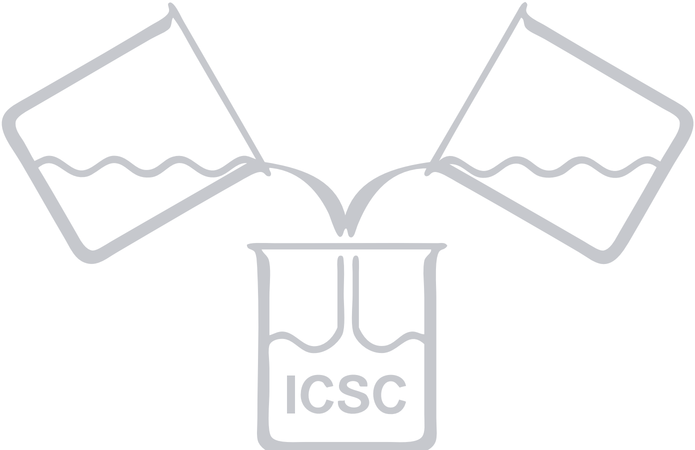
D.
SUPRAMOLECULAR ASSEMBLIES AND NANOSTRUCTURES

Oral Presentations



Fluctuations and Scattering Phenomena in Liquids: Theory and Applications to Studying of Supramolecular Assemblies with Long-Ranged Molecular Correlations

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The problems on describing of non-equilibrium fluctuations in framework of the concept of internal variables with emphasis to studying light scattering phenomena and supramolecular ordering in liquids are discussed.

The thermodynamic potentials of the non-equilibrium states of a matter characterized by the internal parameters of different nature and tensor dimension, which describe both isotropic and anisotropic states have been developed. The expressions for the fluctuating parts of Helmholtz energy F, and Gibbs energy G for the closed systems, as well as the grand thermodynamic potential Ω for the opened non-equilibrium systems, taking into account the scalar, vector, and tensor parameters, were derived.

The contributions from fluctuations of internal parameters to thermodynamic properties (heat capacity, compressibility, thermal expansion coefficient, etc.) as well as the relationships of those with relaxation characteristics are discussed. The relationships between internal parameters and molecular models of liquid systems are discussed.

The theory of integral Rayleigh light scattering, taking into account the effect of the internal field is constructed. The extension of the Lorenz internal field approach for anisotropic fluctuation states is given. The isotropic and anisotropic parts of the permittivity (refraction index) have been subdivided. It was shown that effects of internal field are expressed by the same expression both to isotropic and anisotropic light scattering.

As to isotropic fluctuation and light scattering the revealed correlation of the density and concentration fluctuations in mixtures is discussed. The new contributions to Rayleigh light scattering due to fluctuations of the internal parameters were founded.

Theory of anisotropic light scattering both in pure liquids and mixtures is constructed. The expressions derived relate the Rayleigh light scattering to structural parameters of supramolecular ordering and thermodynamics of aggregation.

The results on studying structural and thermodynamic parameters of aggregation due to noncovalent intermolecular interactions like H-bonds from light scattering data as well as by thermodynamic, dielectric, diffraction, and spectroscopic techniques with emphasis of long-ranged molecular correlations are discussed.

Acknowledgement. This work was supported by the Russian State Support Program of Leading Research Schools (Project № 1275.2003.3) and the Russian Foundation for Basic Research (Project N 04-03-32819).

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X-Ray Diffraction Characterization of Self-Assembled Supramolecular Metallocyclic Species in Solution

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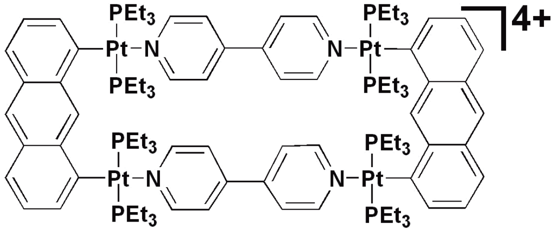
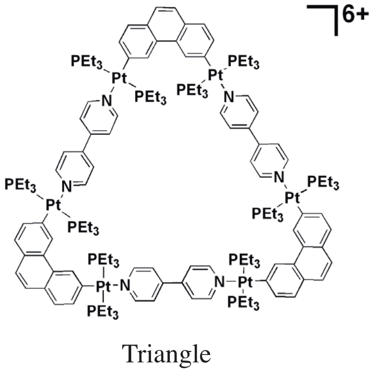
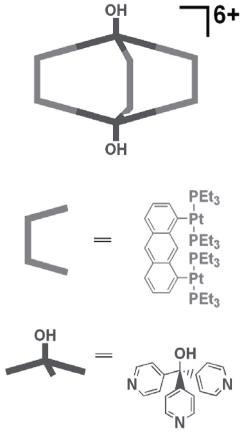
Wide-angle X-ray scattering has been used to obtain structural information on three self-assembled metallacyclic supramolecular complexes in solution, a rectangle, a triangle and a 3-diminsional cage. The low angle region of the measured diffraction patterns, compared to scattering curves derived from the single crystal X-ray diffraction data, suggests the supramolecular assemblies retain their shape when dissolved in nitromethane. The experimental structure functions for the large angle region have been analyzed and the intramolecular contributions of the platinum-platinum interactions are discussed. These scattering measurements provide evidence that the supramolecular assemblies are not as rigid in solution as they are in the single crystal. Finally, by analysis of the radial distribution functions of the solutions, direct structural information (e.g., platinum-platinum intramolecular distances and coordination number) for the supramolecular assemblies have been determined.



Rectangle



Triangle



3-dimensional cage

Phosphorilated Calix[4]arenes as Receptors for Amino Acids Calorimetric and Spectroscopic Experiments

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Thermodynamics of phosphorylated calixarenes interacting with sixteen amino acid residues has been studied using isothermal titration calorimetry. The goal of the research was the complexation analysis between derivatives of 5,17-bis(dihydroxyphosphoryl-hydroxymethyl)-25,27-dipropoxycalix[4]arene and amino acids using model system for Host-Guest interaction.

A moderate variation in the changes of enthalpy, entropy and Gibbs energy for the interactions calixarene-amino acids depending on the nature of both, host and guest were observed. The changes of enthalpy of –14 : -2 kJ mol^{-1} were evaluated experimentally by ITC. The small variations in Gibbs energy in the range of –25 : -20 kJ mol^{-1} were attributed to the effect of compensation enthalpy-entropy. The determined thermodynamic parameters were found to correlate with the hydrophobicity of amino acids, indicating the role played by hydrophobic interactions.

The complexing abilities of phosphorylated calix[4]arenes for amino acids were investigated by a variety of techniques. Calorimetric measurements were carried out to derive the thermodynamic parameters (ΔH, K) of the analyzed complexes. To obtain structural information about the interaction,1H NMR studies were performed. Both NMR and UV-Vis spectrophotometric measurements were used to establish the stoichiometry of the amino acid-calixarene complexes in methanol. The molecular modelling was used to obtain structures of complexes.

The results obtained from calorimetric titration are in good agreement with the suggested interaction pattern determined from 1H NMR experiments as well as UV spectrophotometric titration. The results proved the formation of 2:1 and 1:1 complexes. The experimental data indicated that the Host-Guest complexation was under control of the direct electrostatic interaction between the ionised phosphoryl group(s) located on the upper rim of calixarene with the positively charged amino group of the zwitterionic form of amino-acid residue, and modulated by the hydrophobic interaction, which drive the inclusion of the residue alkyl side-chain into the calixarene cavity. The stability of the inclusion complexes was thus correlates with the length of the aliphatic amino acid's side-chain.

The 1:1 complex was found both entalpically and entropically stabilised. The latter indicates the desolvation of charged groups upon complexation. The 2:1 complex is favourised by positive entropy change strongly correlated with the size of amino-acid residue size. The positive enthalpy change indicates unfavourable electrostatic interaction of two charged calixarene molecules in the complex.

The determination of the two binding modes was possible on the basis of NMR titration experiments,[1] in which 1:1 and 2:1 complexation processes were observed independently on calixarene and amino-acid side-chain resonances, respectively.

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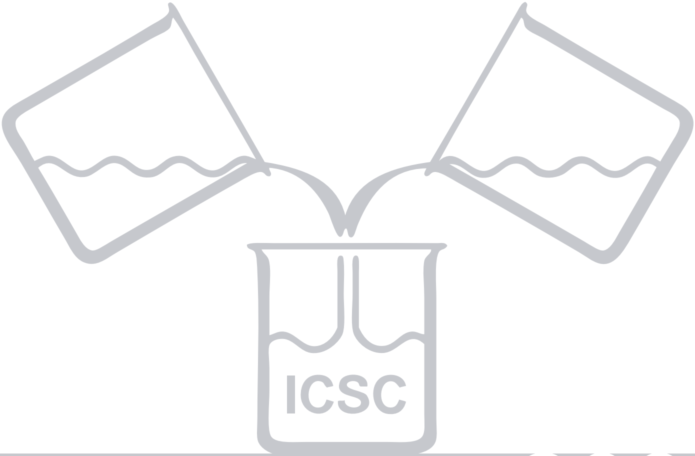
D.

SUPRAMOLECULAR ASSEMBLIES AND NANOSTRUCTURES

Poster Presentations



Nanosized Nickel Oxide Thin Films for Electrochromic Application

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Due to its excellent optical and electrical properties, nickel oxide thin films have been widely studied as an optical active layer in electrochromic devices.[1] Under anodic potentials they change colour from transparent to deep brown.[2] The magnitude of the optical modulation during the colouring/bleaching process depends strongly on a degree of thermal treatment of these films. Too high processing temperature significantly lowers the electrochromic effect[3] and in thermally untreated films the optical modulation decreases soon after the beginning of cycling.[4]

The aim of our work was to optimise the thermal treatment of sol-gel derived nickel oxide thin films, prepared from nickel sulphate, nickel acetate and nickel chloride precursor, on the basis of thermogravimetric analysis of thin films themselves. Nickel hydroxide was precipitated from the precursor solution using lithium hydroxide and the slurry was then peptized with acetic acid. Thin films were deposited on substrates using the dip-coating technique.

Time dependence of the isothermal weight loss of thin films prepared from nickel sulfate (acetate, chloride) precursor via sol-gel route helps us to prepare thin films with different stoichiometry between thermally undecomposed amorphous phase and nano-sized nickel oxide. Isothermal temperature can be chosen on the basis of dynamic measurements. It is 270 °C for thin films prepared from $NiSO_4$ precursor, 230°C in case of $Ni(CH_3COO)_2$ and 200°C for $NiCl_2$ precursor. Results obtained for the corresponding xerogels could not be used because higher decomposition temperature was determined in the latter case. During isothermal treatment the combustion of acetate groups, which are present in all three samples due to peptisation of the gel with acetic acid, takes place and nickel oxide is being formed.[5,6]

It is evident from in-situ spectroelectrochemical measurements that the ratio between thermally undecomposed amorphous phase and nickel oxide is decisive for the electrochromic response and stability of these films during cycling in alkaline electrolyte. Before isothermal treatment the optical response shows irreversibility for the process $Ni^{2+} \leftrightarrow Ni^{3+}$. But different electrochromic behaviors were observed for sulfate (acetate, chloride) thin films isothermally treated to the similar extent. In the case of a sulfate precursor the best properties up to 100th cycle are possessed by a thin film, in which thermal decomposition of acetate groups is complete (60 min at 270°C). TEM micrograph shows that thin film consists of nano-crystals of cubic NiO with a size of 2-3 nm having monodentately coordinated sulfate groups (IR spectrum). The change in transmittance at $\lambda = 480$ nm for this film in the 100th cycle is 46 %. For the acetate precursor optical reversibility is already achieved in a film thermally treated at 230°C for 15 min (25 % decomposition). The monochromatic transmittance change is 40 % in the 100th cycle, but greater differences between these two films are observed at the beginning of the cycling, where the optical response of the latter is very small (11 %). Optimized EC response of thin films, prepared from nickel chloride precursor, was achieved for a film, thermally treated at 200°C for 45 min (13 % decomposition), with a change in transmittance in the 100th cycle of 36 % ($\lambda = 480$ nm). The colouration efficiency of the optimized films was around 40 cm^2 C-1. Structural evolution during thermal treatment was followed using EXAFS and IR spectroscopy, while morphological changes of the thin film surfaces was evaluated with AFM technique.

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Interaction of Porphyrins with PAMAM Dendrimers in Aqueous Solution

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Aggregation of meso-substituted porphyrins (Fig. 1) and their binding to PAMAM dendrimers[1] in aqueous solution is controlled mainly by electrostatic forces. At neutral pH anionic porphyrins (TPPS and TPPP) are bound to PAMAM dendrimer, generation 5 (G5 with 128 amine terminal groups) and cationic porphyrins (TMPyP and TPPTP) to PAMAM dendrimer, generation generation 4.5 (G4.5 with 128 carboxyl terminal groups).

High positive charge of G5 induces preferably the formation of H-dimers and small H-oligomers of anionic porphyrins with face to face arrangement of porphyrin units at porphyrin/G5 ratio greater than 1. The binding can be finely tuned by peripheral substitution of porphyrins and pH. Decrease of pH leads to the protonation of tertial amines inside G5 and then to higher affinity of anionic porphyrin to form H-aggregates. Protonation of porphyrin rings takes place in acidic solution (pH below 2.5). TPPS with negatively charged sulpho groups forms side-by-side J-aggregates, TPPP with fully protonated phosphate groups is transformed to J-aggregates with more random arrangement of porphyrin units. Whereas TMPyP at neutral pH are bound to G4.5 in monomer form, TPPTP extensively aggregates on the negatively charged G4.5 surface. The structure of TPPTP aggregates is similar to that aggregates formed by salt-induced aggregation in aqueous solution[2]: sandwich type H-aggregates, pure J-aggregates with side-by-side arrangement and J-aggregates with more random arrangement of porphyrin units.

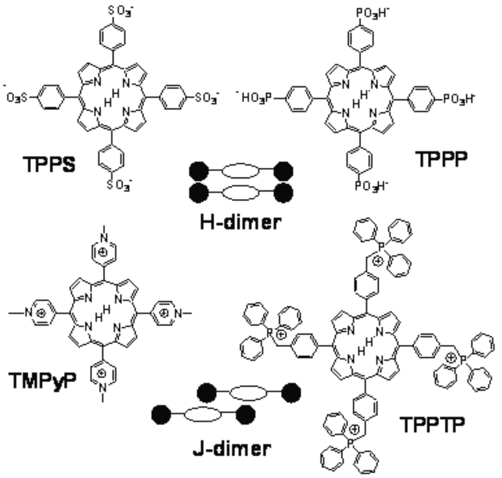

Figure 1. Structure of meso-substituted porphyrins: meso-tetrakis (4-sulphonatophenyl)porphyrin TPPS, meso-tetrakis(4-phosphonatophenyl) porphyrin TPPP, meso-tetrakis(N-methyl pyridyl) porphyrin TMPyP and meso-tetrakis(triphenylphosphonium tolyl) porphyrin TPPTP

Acknowledgement. The research was supported by the Grant Agency of the Czech Republic (Grant No.203/04/0426).

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Complex Formation of Neodymium, Europium and Erbium Nitrates with Neutral Nitrogen-Donor Ligands

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Elucidation of the reasons determining the complex formation lanthanide nitrates in solutions so factors as dipole moment, donor capacity, mono- and bidentate of the ligand molecule, the molecule structure doing the steric barrier, dielectric constant, viscosity and basicity of the solvents is the aim of this study.

The donor capacity of such ligands as 1,10-phenantroline, quinoline, benzoquinoline and ethylenediamine (the data on pyridine from literature) was determined. The 1,10-phenantroline has the less donor capacity, but the ethylenediamine has the most donor capacity.

Synthesis of the lanthanide nitrates complexes with 1,10-phenantroline was carried out. All complexes was isostructural by all lanthanide series in spite of the large difference of crystallochemistry of the initial nitrate crystallohydrates. Only the europium and erbium complexes had the new crystalline phases. The stability of the all complexes was determined by thermogravimetry. Method of synthesis of the anhydrous lanthanide nitrates from the phenantroline complexes was suggested.

The solubility of anhydrous lanthanide nitrates in the ethylenediamine, quinoline, dimethylsulfoxide and the phenantroline complexes in dimethylsulfoxide were determined.

The complex formation in solutions was studied by the IR-, Raman- and NMR- spectroscopy methods. The crystalline phases were investigated by RSA-method.

The nitrate groups of all complexes were found in the first coordination sphere of lanthanide ion. The phenantroline complexes have the most stability. Two molecules of 1,10 phenantroline were situated in the coordination sphere of lanthanide ions. The explanation for it is connected with the large dipole moment of the phenantroline molecule, with the bidentate ligande in complex formation, with the structure of molecule, with the distance between N atoms in the molecule of phenantroline. In general the analysis of literature data and our results leads us to conclution about the better complexation lantanide ions with the oxygen donor ligand but not with the nitrogen donor.

Acknowledgement. Study was supported by Russian Foundation for Basic Research (grant 03-03-32836) and grant of Department of Chemistry RAS ZBO-1.9.

Broadband Acoustic Spectroscopy of Self Organized Structures in Solutions

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The effect of the addition of n-butanol on the micellization of sodium dodecylsulfate (SDS) has been investigated using ultrasonic relaxation method. Measurements acoustic spectra (0,3 MHz – 500 MHz) of SDS-n-butanol-water solutions have been carried out in a alcohol concentration range between $0 \leq x \leq 60$mM and a temperature range $25^{o}C \leq T \leq 55$ ^{o}C. The excess attenuation spectra of the SDS-n-butanol-water solutions reveal two relaxation processes, both characterized by a discrete relation time. Analyzing measurements results obtained characteristic times of enter/exit time surfactant monomer and alcohol molecules into micelles.

Supramolecular Assemblies in the MI_2–$CO(NH_2)_2$–I_2–H_2O Systems (M = Mn, Fe, Co, Ni)

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Numerous complex iodides and polyiodides crystallize from aqueous solutions, containing metal iodide MI_2 (M = Mn, Fe, Co, Ni), urea (Ur), and iodine. The maximal number of complex iodides and polyiodides is found in the MnI_2–Ur–I_2–H_2O system: $[Mn(Ur)_4(H_2O)_2]I_2$, $[Mn(Ur)_6]I_2$, $[Mn(Ur)_6]I_2\cdot 4Ur$, $MnI_2.2I_2\cdot 8H_2O$, $[Mn(Ur)_6][I_8]$, and $[Mn(Ur)_6][I_3]_2\cdot 2Ur$. Only two complexes are formed in the reactions of FeI_2 with urea and iodine in aqueous solution: $[Fe(Ur)_6]I_3$ and $[Fe(Ur)_6][I_3]_3$. In the CoI_2–Ur–I_2–H_2O system, the following complexes are found: $[Co(Ur)_2(H_2O)_4][CoI_4]\cdot H_2O$, $[Co(Ur)_4(H_2O)_2]I_2$, $[Co(Ur)_6]I_2\cdot 4Ur$, $[Co(Ur)_6][I_8]$, and $[Co(Ur)_6][I_3]_2$. The $[Ni(Ur)_4(H_2O)_2]I_2$, $[Ni(Ur)_6]I_2\cdot 4Ur$, $[Ni(Ur)_6][I_8]$, and $[Ni(Ur)_6][I_3]_2$ complexes crystallize in the NiI_2–Ur–I_2–H_2O system. In this work, the structures of the complexes are discussed in terms of supramolecular assemblies.
In the structures of $[M(Ur)_6]I_2\cdot 4Ur$(1) (M = Mn, Co, Ni), the urea complexes form columns, and the iodide ions form zigzag chains running in the same direction; the outer-sphere urea molecules are united in columns containing both dimers and monomers.

The crystals of $[Mn(Ur)_6]I_2$ have a layered structure. The layers of complex cations alternate with the iodine-containing layers, consisting of six-membered rings. The layered structure is stabilized by hydrogen bonds. The complexes with lower urea content (MI_2 : Ur = 1 : 1 and 1 : 4) form supramolecular assemblies with layers consisting of alternating columns of cations and anions; the adjacent columns are combined by the system of hydrogen bonds. Addition of urea to the saturated solution of iron(II) iodide caused oxidation of the metal ion resulting in crystallization of the $[Fe(Ur)_6]I_3$ complex. Increase of iodine content in the solid, as compared to $[Mn(Ur)_6]I_2$, leads to formation of another supramolecular assembly. The crystals of $[Fe(Ur)_6]I_3$ have a stacked structure. The stacks of the iodide ions form channels with a hexangular section accommodating the stacks of complex cations, which form hydrogen bonds with iodide ions building the walls of the channels.

In the crystals of $[M(Ur)_6][I_3]_2\cdot 2Ur$ (M = Mn, Co, Ni), the triiodide anions form stacks combined an layers. The iodine-containing layers alternate with the layers formed by the columns of urea complexes and outer-sphere urea molecules. The crystals of $[Fe(Ur)_6][I_3]_3$ contain no outer-sphere urea molecules; the triiodide ions are united in zigzag chains oriented in such a manner that they form hexahedral channels, which accommodate the octahedral metal complexes. In $[M(Ur)_6][I_8]$ (M = Mn, Co, Ni), the iodine-containing anions are united not in chains but in the fused six-membered rings.

In the MI_2–Ur–I_2–H_2O systems, water, urea and iodine molecules compete in structure formation of the complexes crystallizing from saturated solutions. At low concentration of iodine, urea is believed to be the initiator of formation of the supramolecular assemblies. However, at higher content of iodide ions and iodine, the main role in structure formation passes from urea to iodine. The increase of iodine content leads to exclusion of the outer-sphere urea molecules or inner-sphere water molecules, the polyiodide ions uniting in infinite chains and even in fused rings.

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Structural Properties of Pure Simple Alcohols: Small Angle X-Ray Scattering and Monte Carlo Studies

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The microemulsion systems, i.e. the transparent, isotropic and thermodynamically stable liquid systems with its inner structuration in the colloidal domain, have been substantially studied over the last decades. They consist of water component, oil component and the surfactant, which forms the interface area between the two otherwise immiscible components. To improve the efficiency of the surfactant in microemulsions usually the co-surfactants are added to the system. Higher simple alcohols are frequently used for this purpose. Some interesting features have been observed in the small-angle X-ray scattering (SAXS) spectra of the alcohol rich microemulsion systems in the intermediate q-regime.[1,2] Similar features were expressed also in the SAXS spectra of pure simple alcohols indicating that the inner structuration of the alcohols plays important role in the structuration of the corresponding microemulsion systems. Consequently the inner structuration of the pure liquid alcohols deserves some more attention. As known, the structure of the liquid simple alcohols is governed by hydrogen bonding between the neighbouring alcohol molecules. We compare the structural details as obtained by small-angle X-ray scattering to the scattering curves calculated by Monte Carlo simulations of the model linear alkanols.[3] For the alcohols from ethanol to hexanol, the calculated scattering functions agree very well to the experimental SAXS data. The scattering contributions caused by the individual atom pair arrangements are also analysed. This way, the origins of the peaks that appear in the scattering curves are determined.

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Small-Angle Scattering of Interacting Particles: Ternary Systems of Nonionic Surfactant Brij 35, Water and Various Simple Alcohols

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Structural properties of ternary systems composed of nonionic surfactant dodecyl-poly(ethylene oxide-23) ether (C12E23, commercial name: Brij 35), water and various alcohols from ethanol to 1-decanol have been investigated using small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS) techniques. All measurements were performed at the temperature 25°C. SAXS experimental data were put on absolute scale using water as a secondary standard. The present investigation continues the structural study of the Brij 35/water and Brij 35/alcohol binary systems reported previously.[1-3] Namely, the self structuring ternary systems, often addressed as microemulsions, usually show very complex structural behaviour that can easier be followed if one imagines them as being evolved from the less complicated binary systems with gradually substituting one of the two components with the third one. The data of water-rich mixtures at low to moderate surfactant concentrations were evaluated using the generalized indirect Fourier transformation method (GIFT), which is based on the simultaneous determination of the intra- and interparticle scattering contributions. In this way, the size and the shape of interacting scattering particles in real space could be deduced. The systems with a relatively low surfactant concentration (5 mass %) were studied the most extensively. In these cases, the water-rich regions of the phase diagrams could be investigated into more detail, since in the alcohol-rich regions problems with the GIFT evaluation of the SAXS data were encountered. This study demonstrates the level of structural details that can be obtained on the basis of scattering methods and point out the specific stages of data evaluation and interpretation where one must be extremely precautious. The results reveal the inner structuration of the complex ternary systems of our present interest. In parallel, they also indicate that the longer chain alcohols actually behave as real oil phases in the studied systems, as one might expect, and also confirm the well-known properties of different short to medium chain alcohols that act as co-solvents and/or co-surfactants in microemulsion systems depending on their chain length.

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Simulation Insights on the Structure and Energetics of Biocompatible Polymer Nanocomposite Systems

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The structural arrangement and dynamical behavior of H_2O molecules, ions, and other molecular species in the confined spaces of nano-scale pores and mineral interlayers are key to understanding transport and reactivity in many technological and biological systems. In this respect, considerable research efforts have been focused on the design of nanoscale oral sustained- and controlled-release drug delivery systems.[1] Special attention has been given to finding a way to regulate the rate of drug release by means of monolithic devices where the drug is dispersed or included in an inert matrix.[2,3] A way to produce inclusion compounds with drugs is given by their intercalation in a lamellar host lattice. Recently, for instance, it has been shown[4] that Mg-Al-hydrotalcite (HTlc), an inorganic and biocompatible anionic layered solid, can intercalate two well-known non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen and diclofenac, and modify their release.

In order to couple these features with enhanced mechanical properties in systems to be exploited, for instance, as degradable polymeric implants that can also be used simultaneously to deliver therapeutic drugs to treat infections, polymer clay nanocomposite loaded with NSAIDs can be designed.

Based on our experience in the field,[5-7] in this work we present the results obtained from the employment of atomistic computer modeling to investigate the structure, morphology, and energetics of two different polymer nanocomposite systems based on the two NSAIDs ibuprofen and diclofenac, hydrotalcite and two different biocompatible polymers, poly(□-hydroxybutyrate) and poly(vinyl alcohol).

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Complexation of the Upper Rim Phosphorylated Calix[4]arenes with Uracil Derivatives in Water Containing Solution

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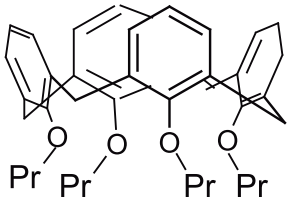
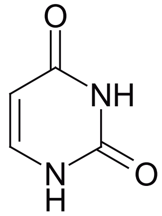
The host-guest complexation of the upper rim diisopropoxyphosphoryl derivatives of dipropoxy- or tetrapropoxycalix[4]arenes as well as the upper rim unsubstituted calixarenes with uracil, 5-chloro-, 5-nitro-, 6-methyl-, 6-amino-1,3-dimethyl-uracil in methanol/acetonitrile/tetrahydrofuran/water (15:10:5:70 v/v) solution was investigated by the reversed-phase high performance liquid chromatography[1,2]. The binding constants of the 1:1 host-guest complexes were in the range of 1500 to 54000 M^{-1} and they were found dependent on the conformation and stereochemical mobility of the calixarene skeleton, number of the phosphoryl groups at the upper rim, as well as nature of the guest. Molecular dynamic (MD) simulation of host-guest interaction was performed. Basing on the MD trajectories atomic partition to the net molecular solvent-exposed surface was analyzed for the separated host and guest molecules and for the complex. Hydrophobic effect, NH-π interactions in the complexes was investigated by molecular modelling.

Host - phosphorylated derivatives of tetrapropoxycalix[4]arene (left), and Guest -derivatives of uracil (right) formulas are presented in the scheme below.





The strong binding is observed for the derivatives of tetrapropoxycalix[4]arene functionalized at the upper rim with hydrophilic proton-attractive diisopropoxyphosphoryl groups. The phosphoryl groups weaken complexation with uracil and adenine derivatives in the case of the stereochemically flexible tetraprapropoxycalix[4]arene, but increase the complexation for stereochemically rigid dipropoxycalixarenes. For all of the analyzed complexes, the uniform pattern of Host-Guest interaction, including hydrophobic and π-π interactions, NH-π, CH-π binding and Van der Waals forces play an important role in the complexation process. The experimental results determined with the aid of HPLC retention measurements are in good agreement with the structural data obtained using molecular modelling.

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E.

ANALYTICAL AND ENVIRONMENTAL ASPECTS, AQUATIC CHEMISTRY

Oral Presentations

Thermodynamic Data for Carbon Dioxide Dissolution in Aqueus NaCl Solution

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The carbon dioxide (CO_2) is the principal cause of the so-called greenhouse effect, leading to global warming. The emission of acid gas, resulting from the combustion of fossil fuels, i.e. Oil or coal, or present as constituents of natural gas, must be reduced. A procedure consists in the capture, the transport and finally the geological storage of acid gases in depleted oil or gas reservoirs, unminable coal beds or in deep saline aquifers. Calorimetric measurements can be useful in obtaining the thermodynamic data necessary for modelling gas sequestration in saline aquifers. In this connection a flow technique[1,2] was developed to measure the heats ofsolution of a gas in a liquid in temperature range from 298 to 473 K at pressures up to 40 MPa. The measurements are performed with an isothermal differential heat flux calorimeter, equipped with a customized mixing cell. It allows simultaneous determination of the heat (enthalpy) of solution and of the gas solubility inthe liquid phase. The study has been performed for dissolution of CO_2 in water and aqueous solutions of sodium chloride (NaCl), between 1 mol.kg^{-1} and 3 mol.kg^{-1}, at temperatures 323 K and 373 K and pressures upto 20 MPa. The influence of pressure and salt concentration is documented by changes in the heats of solutionand the solubility limits of carbon dioxide. The solubility values obtained from the analysis of the calorimetricsignal are compared with recent direct experimental data[3] and computed values obtained from a correlation.[4] The reasonable agreement suggests that this technique, besides being a reliable source of enthalpic data, is alsosuitable for the indirect determination of solubility. The enthalpy of hydration ΔH_{hyd} at the pressure of 0.1 MPa of water has been derived from the enthalpies of solution, using the residual enthalpies of pure solute $\Delta H^{*}_{\text{res}}$ and solute in the state of infinite dilution[5] $\Delta H^{\infty}_{\text{res}}$. A good consistency has been observed with the enthalpy of hydration obtained from the temperature derivative of the Henry‘s law constant.[5,6]

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Macroaggregates in the Northern Adriatic Sea

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The hyperproduction of mucous macroaggregates in the northern Adriatic Sea, usually observed during the late spring-summer, are rather frequent event in the last sixteen years. Mucous macroaggregates are defined as macrogels produced by phytoplankton. Its formation includes processes transforming macromolecular dissolved organic matter (DOM) into colloidal organic matter (COM) and successively into particulate organic matter (POM). The most important source of COM are phytoplankton-derived colloids mostly originating in phytoplankton exudation (polysaccharidic) and cell lyses. Spectroscopic studies (^{1}H and ^{13}C-NMR, FT-IR) showed that the northern Adriatic macroaggregates are mostly composed of carbohydrates, aliphatic chains, organosilicon compounds and inorganic fraction including calcite, quartz and clays (Kovac et al, 2002).

The aggregation process could be explained via polymer gel theory (Chin et al, 1998) and the formation of nanogels and further of microgels (Verdugo et al., 2004) that continue to agglomerate in particulate organic matter (POC). Accordingly to the trends of dissolved organic matter to be concentrated at phase boundaries, such as the sediment-water, air-sea interfaces, pycnocline and due to the presence of mineral particles (sediment, atmospheric dust), the COM and mucous macroaggregates agglomerate and further accumulate in those layers. The transformation of DOM to COM include the increase in size and changes in reactivity of material. Photopolymerization, leading to the high molecular organic matter, seems also important as transformation process of COM. The high molecular weight of water-soluble fraction of mucous macroaggregates was confirmed by the size exclusion chromatography (SEC). Macromolecules represent the substrate less available to bacteria and so they could concentrate. The isolation of the northern Adriatic Sea with special physical summer condition (development of pronounced pycnocline and, stable summer conditions with low turbulent sher) additionally enable subsequent concentration and agglomeration of macromolecular organic matter (and phytoplankton cells in the presence of mineral particles). The mineral particles and/or ions such as Ca^{2+} and Fe^{3+} seem to be very efficient cross-linkers (Verdugo, 1994; Chin et al., 1998) between marine hydrogels. This was confirmed by laboratory experiment showing that flocculation of gels into macrogels started immediately after the addition of calcite, silicates and $FeCl_3$ from seawater ("supersaturated gel solution") at the beginning of mucous appearance (Kovac et al, 2002).

The increased assembly rates of marine gels leads to an increase of POM (Verdugo et al., 2004) i.e. larger particles that contribute to clarification of the sea water column which was usually observed before the greater macroscopic mucous appearance. In this case, mucous macroaggregates play an important role in scavenging processes and further in transformation of marine organic matter.

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Analytical Studies and Flow Injection Methodological Speciation of Iron in the Water Samples from Bastar District, Chhattisgarh State, India

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Analytical studies and flow injection methodical speciation of iron were carried out in ground water (tube well) samples collected from the Baster district (18° - 21° N latitude and 80°17’ - 84°11’ E longitude) of Chhattisgarh State, India. This study involves the collection of ground water samples (n = 75) from the study area and monitoring of their pH, conductivity, and speciation of Fe (Total, ferrous and ferric) concentration. The speciation of iron was carried out by using established flow injection analysis method based on the measurement of the colour of the complex formed with thiocyanate ion, cetylpyridinium chloride (CPC) and 2,2’- bipyridine (BP_y) in the acid ($HCl + H_2SO_4$) medium. Total iron concentration was determined by adding 0.2 ml of the concentrated nitric acid to the filtered water sample, prior to the analysis. The concentration level of the ferrous iron in the water sample was determined by subtracting the value of concentration of ferric iron to the concentration of total iron. The concentration of ferrous, ferric and total iron in the ground water samples were found in the range of 0.015 – 0.365 μg mL^{-1}, 0.010 – 0.150 μg mL^{-1}, and 0.025 – 415 μg mL^{-1}, respectively. The pH and conductivity of these samples collected were found in the range of 5.15 – 8.03 and 0.05 – 1.10 m. mho, respectively. The ground water of the study area was found to be generally colourless but become opalescent when comes in the contact with air and useless for domestic purposes. This opalescence may be due to the oxidation of Fe^{2+} into Fe^{3+} and their subsequent further hydrolysis into hydrated oxides.

Features of Nitrates Extraction From Drinking Water by Anion Exchange Resins

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The high level of nitrates in drinking water represents the serious hazard for people health. The allowable limit of nitrates concentration in drinking water is regulated by requirements of country standards and should not exceed 45 mg/L in Ukraine[1] or 50 mg/L for the majority of countries.[2] For water used for beverages preparation these requirements are more rigid.

In Ukraine drinking water is supplied by both centralized and local water supply lines. The concentration of nitrates in water of the central supply system provided by superficial sources (rivers, lakes) or deep wells usually does not exceed 10 mg/L. However, in water of local shallow wells the nitrate level can achieve 300 mg/L and more. The penetrations of industrial wastes (such as drains of the cattle-breeding enterprises, fertilizers, waste products of a war industry etc.) into soil waters are the traditional sources of water pollution by nitrates. The sorption method based on use of the strong base anion exchange resins usually applies to remove nitrates from water. The essence of a method consists in ability of the strong base anion exchange resins to absorb nitrates ions from water, replacing chlorides - ions.

However, at use of the specified method it is necessary to note that sulfates and hydrocarbonates are absorbed with nitrates simultaneously, as well as chlorides are desorbed. Affinity of the standard strong base anion exchange resins to nitrates is always lower than to sulfates. As a result the part of resin capacity is spent for sulfates and nitrates at the filling of functional groups are superseded by sulfates, and their concentration in water sharply raise up to a level exceeding initial. The special nitrate-relationship anion exchange resins differed by a matrix nature are produced now and their affinity to nitrates are higher than to sulfates. Within the framework of researches the sorption-desorption processes of nitrates extraction from waters with various ratio of nitrates and sulfates were investigated for both standard anion exchange resins and nitrate-relationship anion exchange resins, and capacity characteristics of resins were determined.

The outlet curves received as a result of researches have shown that the using of nitraterelationship anion exchange resins excludes an opportunity of increase the concentration of nitrates in the purified water above an initial level. However these anion exchange resins are characterized by lower values of total ion exchange capacity, and higher price than standard resins and therefore the processes based on their use are more expensive.

Working dynamic capacities for both standard and nitrate-relationship anion exchange resins are determined at their use in a mode "sorption-regeneration". As a result the conditions of preferable ranges for use of every type of ion exchange resins for extraction of nitrates from waters with various compositions are formulated. Formulas for calculation of working capacity of anion exchange resins to nitrates are suggested and then confirmed by pilot tests. The determined characteristics allow to calculate successfully parameters of installations for purification of water with various composition and ratio of nitrates and sulfates.

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Energy Transfer from Mixed-Ligand Complex of Ruthenium(II) to Chromate(III) Complex in Aqueous Solution

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Luminescence from ^{3}MLCT state of ruthenium(II) complexes is quenched by chromate(III) complexes in crystal and solution. The quenching is brought about by energy transfer from ^{3}MLCT state of ruthenium(II) complexes to ^{2}E state of chromate(III) complexes. In crystal, the energy transfer is much affected by relative geometry between donor- and acceptor-complexes.[1,2] In aqueous solution, the quenching rate constants obtained by Stern Volmer Plots of luminescence lifetime of donor complex are much smaller than the diffusion rate constants. Thus, the energy transfer occurs in encounter complex of the donor and acceptor. The energy transfer is affected by co-existing alkali cations.[3,4]

The effect of ligands coordinating to metal ion on the quenching reaction of excited $[Ru(N-N)_2(N-N)']^{2+}$ (N-N = 1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridine, 2,2'-bipyridine) by $[Cr(CN)_6]^{3-}$, $[Cr(ox)_3]^{3-}$ ($ox^{2-} = (COO^-)_2$) and $[Cr(mal)_3]^{3-}$ ($mal^{2-} = CH_2(COO^-)_2$) in aqueous solution was studied. The quenching is also brought about by energy transfer from ruthenium(II)- to chromate(III)-complexes. The energy-transfer rate-constants were evaluated with quenching-, diffusion- and dissociation-rate constants. The relation between energy-transfer rate-constants and ligands of ruthenium(II)- and chromate(III)-complexes is discussed. Moreover, the structure of encounter complex in aqueous solution will be also considered.

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XAFS Studies of Pd(II) Complexes in Concentrated Nitric and Perchloric Acid Solutions

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Despite of XAFS technique overall success, the picometer barrier (10^{-2}Å) exists in an XAFS data analysis. Recently we have demonstrated that high accuracy XAFS measurements and new XAFS data analysis procedure allowed obtain local structural parameters with psubpicometer accuracy.[1,2] Here we present a comparative XAFS analysis on $Pd(H_2O)_4^{2+}$ complex and the mixed nitric $Pd(NO^3)_2$ $(H_2O)_2$ complex in solutions with subpicometer accuracy. Structural parameters of the $Pd(H_2O)_4^{2+}$ complex and the mixed nitric $Pd(NO_3)_2$ $(H_2O)_2$ complex were determined.

For pure 5M $HClO_4$ and for mixtures (0-0.3 M HNO_3), the XAFS spectra of the 0.02 M Pd solutions are indeed very similar and originated from four Pd-O_W equivalent distances. For the $Pd(H_2O)_4^{2+}$ square planar aqua ion in a strong perchloric acid, the use of an FEFF6 theoretical approach led to a first shell Pd-O_W distance of 2.00^1 Å and a Debye-Waller (DW) factor of σ^2=0.0030 (3) Å^2. Four water molecules are tightly bound to the Pd^{2+} ion in the equatorial plane while two (or one) axial water molecules are weakly bound to the metal ion at 2.5 Å with DW factor 0.015 (5) Å^2.

For high concentrated mixtures (4-6 M HNO_3) and for pure concentrated (4-6 M) nitric acid as well as for crystalline powder $Pd(NO_3)_2$ $(H_2O)_2$, the XAFS spectra are very similar and determined by the mixed nitric complex $Pd(NO_3)_2$ $(H_2O)_2$: four Pd-O near equivalent distances of 2.01^1 Å from two H_2O and two NO_3 molecules with total DW factor of σ^2=0.0037 Å^2. Moreover, two Pd--N distances of 2.8-2.9 Å were determined in the second coordination shell.

Finally, for intermediate mixtures (1-3 M HNO_2 in 5M $HClO_4$), the XAFS spectra are superposition of the XAFS of $Pd(H_2O)_4^{2+}$ and $Pd(NO_3)_2$ $(H_2O)_2$ complexes. The mean ligand number NO^{3-} around Pd^{2+} has been calculated and the XAFS results, at pH close to zero, confirm the spectrophotometric results previously published.

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Chemical States of Crystalline and Aqueous Solutions of NaBr and NaBrO3 Using *In-situ* Soft X-Ray Absorption Spectroscopy and First-Principles Calculation

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Chemical states of Na^+ and Br^- or BrO^{3-} in the aqueous solution of NaBr and $NaBrO_3$ have been less actively examined because they are considered to have the same states as Na^+ and Br^- in NaCl and LiBr. However, the discussion on the chemical states is insufficient as the difference in coordination number and interatomic distance around Na^+ derived from X-ray and neutron diffraction measurements and molecular dynamics and Monte Carlo simulations has been seen in Ref.[1] The chemical state of BrO^{3-}, in particular, has not reported. In this presentation, we show the the chemical states of cations and anions in the crystalline and aqueous solutions of NaBr and $NaBrO_3$ using a new experimental setup as described below.

The new experimental setup enables to measure in-situ x-ray absorption spectra under ambient conditions in the 400-2000 eV photon-energy region using total-fluorescence-yield detection techniques, and its utility has been demonstrated by studying the metal thin films under the exposure of hydrogen, and electron structure of Br– ion in aqueous solutions.[2,3]

For the XAFS spectral feature of Na K-edge for NaBr, the number of oscillations in crystal is greater than that in solution, and the peak positions in crystal are very different from those in water. This result shows that crystalline NaBr is dissolved in water, and dissociates into Na^+ and Br^- ions, and then they form hydrated structure easily. The EXAFS analysis provides the coordination numbers and interatomic distances for Na^+ ions in the crystalline and aqueous solution of NaBr.

The Br L3-edge XANES spectra for crystalline and aqueous solution of NaBr also differ in the peak position, suggesting that the dissociation of NaBr into Na^+ and Br^- ions occurs in aqueous solution as described above. The XANES spectral features of both Na K- and Br L3- edges for $NaBrO_3$ do not show greater difference in peak positions and oscillations between its crystal and aqueous solution, compared with those of NaBr. This result suggests that $NaBrO_3$ incompletely dissociates into Na^+ and BrO^{3-} ions in aqueous solution.

The ligand field potential (10Dq) observed in the Br L-edge x-ray absorption spectra allows in determining their dependence on the inter-atomic distances between Br and the first near neighbor in crystalline NaBr, and $NaBrO_3$ and the effect of hydration in the corresponding aqueous solutions. The discrete variational(DV) Xa molecular-orbital calculations show the transitions occur from Br 2p to the unoccupied states containing mainly 4d orbitals of Br for both crystalline and aqueous solution, 5s and 5p of Br also contribute to the unoccupied states in addition to the 4d orbitals of neighbour Br due to the orbital mixing in crystalline bromides.

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E.

ANALYTICAL AND ENVIRONMENTAL ASPECTS, AQUATIC CHEMISTRY

Poster Presentations

Carbonate Equilibrium in Aquatic Systems Using Stable Carbon Isotopes

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The carbon cycle plays an important role in controlling many of the chemical and biological processes in different aquatic systems. Many reactions and processes in the water column and sediments are related to fixation of CO_2 to organic matter and its degradation. The concentration of dissolved inorganic carbon in aquatic environments reflects mineralization of organic carbon to CO_2. In carbonate rich sediments the DIC is also influenced by the dissolution and precipitation of carbonate, irrigation by benthic organisms and diffusion from overlaying water column. In this presentation the sources of dissolved inorganic carbon (DIC) in pore waters of three aquatic sediments were determined and compared: coastal marine carbonate rich sediments in the Gulf of Trieste, N Adriatic Sea, sub alpine lacustrine carbonate rich sediments of Lake Bled, Slovenia, and sediments from boreal Lake 658 at the Experimental Lakes Area in northwest Ontario, Canada. For this purpose the isotopic composition of DIC ($\delta^{13}C_{DIC}$) in pore water was coupled with a comprehensive pore water chemistry and sediment environment. The model accounting for diffusion, irrigation, and the remineralization of organic carbon was used to better understand the observed variations in concentration and isotopic composition of DIC.

A model that accurately described the profiles of DIC concentrations in marine sediments could not be used to reproduce the observed isotopic profiles. However, there is a clear indication that the $\delta^{13}C$ of DIC added to the pore water was significantly greater than the $\delta^{13}C$ of organic carbon. Dissolution of $CaCO_3$ was estimated to contribute 35-57% to DIC in winter and late spring and 14% in late summer when the degradation of organic matter was the highest. Another source of ^{13}C-enriched carbon in pore waters might be diffusion of bottom-water CO_3^{2-} into the sediments, or the diffusion of ^{13}C-depleted $H_2CO_3^*$ from pore waters to bottom water.

Using the model the observed isotopic and concentration profiles of DIC in sediments of lake Bled are reproducible. The dominant carbon isotope effect expressed during early diagenesis of organic matter is associated with methanogenesis which proceeds preferentially by CO_2 reduction. The contribution of methanogenesis to the DIC was estimated to be 38-78% using mass and isotopic balances. The highest contribution of carbonate dissolution was observed in the oxygenated part of the lake in spring (12%), characterized by lower bottom water temperatures and slower degradation of sedimentary organic matter. In all other parts of the lake calcite precipitation is thermodynamically favored and therefore, calcite could not represent the source to DIC.

The amount of organic carbon regenerated by methane fermentation which was found to be the predominant way of methane formation in the boreal Lake 658 sediments in Canada was estimated to be between 8 and 78% depending on the temperature and organic carbon input. Modeled profile of $\delta^{13}C_{DIC}$ in the deepest part of the lake 658 did not agree with the concentration DIC data. This indicate that a diagenetic model for isotopic data must include other processes such as oxidation of methane within the sediments. However, it was found that even if the pathways of methane formation are different in soft lakes compared to carbonate rich lakes, the contribution of methanogenesis to DIC is similar in anoxic parts of the lake and represent up to 78% to DIC.

Investigations of the Physicochemical Properties of the Fountain Solutions

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Physicochemical properties of the fountain solutions, such as electrical conductivity, pH value, surface tension and contact angle in dependence of solutions concentration on nonimage areas of the typographical form for offset printing method were estimated. Two samples of typographical form with classical diazo coating and thermal plate coating were used.

The obtained results show that the surface tension of fountain solution decreases by the concentration increase of the fountain solution, while electrical conductivity for fountain solution samples constantly increases.

The dampening process occurs in mild acid medium (pH value is between 5.0 and 5.1), which points out that salts acting as buffers are added to the solution. Contact angle, as a proper moistening measure is being decreased by increasing concentration of fountain solution, enabling good moistening of non-image areas on the printing plate.

Fountain solution successfully moistens the non-image surfaces at the concentration of 30 – 40 vol %. Sample 1 showed best characteristics, because the contact angle is small enough, which indicates a good spreading of the fountain solution across the surface of the printing form, as well as a good wetting as one of the most important factors in plane printing. Presents of surface active substances decreases surface energy of solvents, which decreases contact angle measured on non-image areas.

Contact angle has linear dependence on surface tension for all three examined samples. Sample 1 shows slightly higher values than samples 2 and 3. Linear dependence of contact angle on surface tension shows that there is a good combination of all additives in fountain solution, most of all surface active substances.

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Precipitation of Gypsum from Waste Sulfuric Acid and Lime

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The precipitation of gypsum, from waste sulfuric acid from TiO_2 production plant and pure sulfuric acid, with lime suspension in a continuous pilot plant in the temperature range from 40°C to 80°C, was studied. It was observed that in the case of waste sulfuric acid with a high content of Mg^{+2} and Fe^{+2} ions, several hours after the beginning of the precipitation partial dissolution of the product and modification of the crystals from needle- and plate-like to agglomerated twin structures occurred. The analysis of the degre of superaturation during continuous precipitation process suggests that the secondary changes occur due to the increased concentration of Mg^{2+} and Fe^{2+} ions in the reactor. Below 60°C, plate-like, and above 70°C needle-like single crystals were formed. The mean size of the crystals was found to increase with increasing temperature and decrease with the initial concentration of lime. Gypsum produced between 70°C and 80°C is suitable for further processing to the β form of calcium sulfate hemi-hydrate.

Prediction for Aqueous Solubility of 209 PCB Congeners on the Basis of Computational Neural Networks

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Aqueous solubility coefficient(Sw) of 209 polychlorinated biphenyl(PCB) congeners known as environmental contaminants was predicted on the basis of computational neural networks(CNNs) using a set of information-rich descriptors encoded molecular geometry and electronic properties calculated by using a MOPAC93 Rev.2 program package,[1] for example, heat of formation(DHf), solvent accessible surface area(SAS), energy level of the highest occupied molecular orbital(E_H), energy level of the lowest unoccupied molecular orbital(E_L), dipole moment(m), the sums of the charge at hydrogen atom(QH), and the chlorine atom(QCl) bound to biphenyl skeleton. In addition, gas chromatograph relative retention time(GCRT) was also used as a descriptor.

To form the basis for a CNNs model, logSw of 136 PCB congeners, which had been reported, was used as a training set.[2] The optimum middle layers and learning times were determined in terms of leave-one-out(LOO) cross-validation procedure by back propagation method in Chemish ver. 4.05 software.[3] In this procedure each logSw datum is systematically excluded once from the training set, after which its logSw value is predicted by a model derived from the remaining data. Combining the 136 predictions allows the calculation of a cross-validated r^2 (termed q^2 hereafter). Using the optimum middle layers and learning times, the final CNNs prediction was carried out without cross validation to generate a CNNs model with a conventional correlation coefficient r^2. The r^2 and q^2 parameters are two key measures of significance of the model. The r^2 value is a measure of the model's goodness of fit to the training set while the q^2 value is a measure of the model's predictive ability. A model for which $r^2 > 0.9$ and $q^2 > 0.5$ is generally considered to be both internally self-consistent and prediction.[4]

In first, a CNNs model was constructed for predicting logSw of 209 PCB congeners. This model was regarded as having good self-consistency and predictive ability, because statistical significant values of q^2 (=0.972) and r^2 (=0.982) were obtained, respectively. On the otherhand, we newly constructed CNNs model for predicting logSw of the PCB isomers, since it has been pointed out that the physicochemical properties of PCB congeners are mainly governed by mass-depending parameter such as the molecular weight.[5] For pentachloro biphenyl isomers (28 data number), the statistical significant values of q^2 (=0.831) and r^2 (=0.965) were obtained, and judging from the r^2 values(=0.754) obtained from the congeners' model, the prediction ability(q^2) seemed to be also improved. In addition, it has been known that GCRT is a useful descriptor for predicting the logSw. Therefore, CNNs models including GCRT as the descriptor were constructed. However, no marked improvement for the prediction ability was obtained. This indicates that the use of CNNs has made possible for constructing effective prediction models on the basis of only non-empirical descriptors by using computer-assisted calculation.

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Study of the Adenosine 5’-triphosphate Adsorption Behavior onto Photocatalyst Surfaces in Aqueous Solution

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A study of adsorption behaviour between the surface of photocatalytic powders and photodecomposition materials is very important for the development of new type photocatalysts modified by using some lanthanide ions. In the case of Methylene Blue or Rhodamine B, some kinds of models of adsorption behaviour onto surface of photocatalysts were reported by using Raman and FT-IR measurements.[1] Clearly to evaluate adsorption reaction, however, is too difficult to explain. This study used the new approach for evaluating the adsorption behaviour by using Langmuir isotherm to the dispersion of Adenosine 5’-triphosphate (ATP) and photocatalysts in order to obtain the number of adsorption sites and the adsorption equilibrium constant. Our previous paper[2] about photocatalytic degradations of ATP can let us easily understand the behaviour of the three subunits (adenine-, ribose- and phosphate mieties).

Selected photocatalysts were non-modified titanium dioxide (TiO_2), lanthanide ion adsorption TiO_2 (Ln/TiO_2) and TiO_2 doped by lanthanide ion (Ln-TiO_2). Three ions, Lutetium, Ytterbium and Europium ions which have the unique 4f electron lying close its atomic nuclei were chosen as modified materials. Nominal property in the photocatalytic reaction solutions of Ln/TiO_2 and Ln-TiO_2 powders was different from that of TiO_2, and each powder has the high photocatalytic activity than TiO_2. The ATP decrement in a adsorption reaction solution were detected by means of HPLC apparatus and particle size distribution of each photocatalytic powder in the dry- and wet condition was measured through the courtesy of Sysmex Ltd..

From the result of the plot of Langmuir isotherm and particle size under the dry- and wet condition, the role of the adsorbed lanthanide ion was considered to change the particle size to more small size in the wet condition. On the other hand, the purpose of the doped lanthanide ion was considered not to change the particle size but to increase the photocatalytic activity of TiO_2 in the Ln-TiO_2 powder in wet condition. In this difference this paper will discuss the adsorption behaviour between the surface of photocatalytic powders and ATP in aqueous solution.

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The Study of Water Quality Assessment and Methods of Arsenic Removal

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The present day speedy socio-economic development of humanity has most vigorously stimulated change in nature. Technological advancement, if on one hand has bettered the life of humans on this planet; on the other hand it has sharply intensified the pollution of environment. Industrial waste or effluents seriously pollute most of the Indian rivers, which includes inorganic and organic toxicants. The water treatment has become both an ecological as well as an economic necessity. The investigations over the years have observed that the presence of toxic metals in ground water has manifested itself in various types of disease in human- being and adversely effect the plant growth. So the study of water treatment is of great challenge to the society. The present study summarizes the result of analysis of industrial effluents of sewage draining into Yamuna River, an important tributary of Ganga, in the region of eastern Haryana (INDIA). The concentration of As, Pb, Cr, and Hg has been determined in a large number of industrial waste samples. The sewage samples were collected at regular interval and were analysed for Suspended Solids 248.5(mg/L), BOD 168.9(mg/L), COD 390.0(mg/L), and pH 8.07. The industrial wastes containing toxic metals raises the risks of affecting the quality of water reserves/resources of this area due to percolation of these hazardous pollutants. Arsenic (As) is a metallic element that occurs both naturally and from human activity. Its presence in ground water is largely the result of geo-chemical soil leaching. The paper describes new safe water technologies for As removal, which require several technological criterions. The biggest challenge lies in applying the technologies in socioeconomically backward regions.

Trace Metals and Physico-Chemical Parameters Correlations in Water Reservoir

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Dissolved trace metals concentrations are the consequence of geochemistry of the rocks in the catchment's area, climatic and hydrology, conditions, anthropogenic and other changes. The aim of this work was to analyze the connection between dissolved microelements concentration and physicochemical parameters in the Barje accumulation (located on the Veternica river, 30 km upstream from Leskovac, Serbia; volume of 40.7 millions of m^3) built for water supply. The correlations included two populations: from the inflow sites and from the other accumulation sites. The inflow sites contained much more organic substances than the other sites, which was confirmed by high significant correlations of dissolved trace metals from those sites with COD and BOD. Slightly positive correlations were found between dissolved trace metals contents and concentrations of ammonia, nitrite, phosphate, turbidity and COD.[1] Curved shape correlations suggest a surface adsorption. Dissolved microelements depend of pH and dissolved oxygen concentrations. The vertical distribution of oxidation states of the metals indicates nonequilibrium conditions due to microbiological and chemical processes occurring in the redox transition zone. Near the sediment water interface, anoxic conditions may occur, under which iron and manganese oxides undergo reduction and dissolution.[2] Anaerobic conditions, which may occur in the cooler, lower layer, hypolimnion, may increase metals concentration. Thus negative correlations were found for the correlations of the dissolved trace metals concentrations with pH and dissolved oxygen concentrations. It can be concluded that organic substances play an important role in the mobilization of most trace metals.

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F.
SOLVENTS AND SOLUTIONS UNDER EXTREME CONDITIONS

Oral Presentations

Deficiency and Mobility of Coordinated Water in Crystalline Nonahydrated Scandium(III), Yttrium(III) and Lanthanoid(III) Trifluoromethanesulfonates

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The hydrated scandium(III) and lanthanoid(III) ions, La to Lu, form tricapped trigonal prisms in the isomorphous series of nonahydrated trifluoromethanesulfonates, $[M(H_2O)_n](CF_3SO_3)_3$.[1] Water deficiency occurs randomly in the capping positions for the smallest trivalent ions, M = Er, Tm, Yb, Lu, Sc, n = 8.96(5), 8.8(1), 8.7(1), 8.5(1), 8.0(1), respectively. Hydrogen bonds from the surrounding trifluoromethanesulfonate ions hold the water molecules together pair-wise, stabilizing the trigonal prism. ^{2}H solid-state NMR showed that the coordinated water molecules of the diamagnetic compounds $[M(H_2O)_n](CF_3SO_3)_3$, M = Sc, Lu, Y and La, could exchange positions. Fast positional exchange on the ^{2}H NMR time scale ($>>10^5$ s^{-1}) started at higher temperature for the fully nonahydrated yttrium(III) and lanthanum(III) ions than for the water deficient scandium(III) and lutetium(III) ions. A possible mechanism is discussed. Differential scanning calorimetry (DSC) showed for all the water deficient trifluoro-methanesulfonate compounds reversible phase transitions at about 185 K. Single crystal data at 150 and 100 K showed that the $[Sc(H_2O)_{8.0}](CF_3SO_3)_3$ compound transformed to an almost 9 times larger trigonal cell with the scandium ion surrounded by seven fully occupied oxygen atom positions, and another two distant positions approximately half occupied. By distorting the prism, expanding one side to allow one capping oxygen atom to approach closer while one more distant capping oxygen atom is released, a more stable configuration is achieved around the metal ion. The phase transitions are probably triggered by the instability when the three capping oxygen atoms become strongly repelled by the prism oxygen atoms for the shrinking trigonal prism around the smallest metal ions.

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Standard Partial Molar Volumes in Water of Mono and Polyhydric Aliphatic Alcohols in Wide Ranges of Temperature and Pressure

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New results of a systematic study of partial molar volumes at infinite dilution (standard partial molar volumes) in water of several hydroxyderivatives of aliphatic hydrocarbons are presented. The experiments were performed using an automated vibrating-tube densimeter[1] designed for the measurements of density differences $\Delta\rho = \rho(\text{solution}) - \rho(\text{water})$ in the temperature range from 298 K to 573 K and at pressures up to 30 MPa. The set of solutes comprised monohydric alcohols derived from methane, ethane, propane, and isomers of butane, and selected polyhydric (from two to five hydroxyl groups) derivatives of ethane, propane, n-butane, n-pentane, 2,2-dimethylpropane and n-hexane.

There are two types of the surface of the solute molecule: i) a hydrophobic surface represented by the hydrocarbon part of the molecule, and ii) a hydrophilic surface at the sites of hydroxyl groups. Within a simple consideration we may expect a volume expansion of the hydration shell on the hydrophobic surface compared to the bulk water (i.e., an increase of the partial molar volume) and a volume contraction on the hydrophilic surface (i.e., a decrease of the partial molar volume). Therefore a ratio between hydrophilic and hydrophobic surface area of the solute molecule affects the solute standard partial molar volume. The number and positions of the hydroxyl groups and a shape of the molecule play a role, too.

The experimental results revealed several interesting phenomena.

1. At ambient temperatures the effect of the hydroxyl group is negligible, i.e. the standard partial molar volumes of alcohols with different number of hydroxyl groups derived from the same hydrocarbon (e.g., 1-propanol, 2-propanol, propane-1,2-diol, propane-1,3-diol, propane-1,2,3-triol) are nearly identical. On the other hand, the significant diversity of partial molar volumes is observed at high temperatures where the effect of the hydrophilic character of the hydroxyl group is more pronounced.
2. Increasing area of the hydrophilic surface of a solute molecule, i.e. increasing number of hydroxyl groups, may even result in a change of the sign of the derivatives of partial molar volume with respect to temperature and pressure at high temperatures. A simple group contribution method proved to be capable to predict this behaviour qualitatively, the effect is not, however, strictly additive.

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Physicochemical Features of Lanthanide Halide Molten Salt Solutions

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Heavy elements that have f-electron orbitals, which are called lanthanide and actinide, show particular chemical characteristics under various conditions.

Several research groups worldwide study the chemical characteristics of f-elements under the condition of various liquids, such as aqueous solution, highly concentrated salt solution, molten salt, and liquid metal.

The efforts made in clarifying the chemical phenomena and their mechanisms, are of interest in several fields such as the development of new chemical separation and purification technique for nuclear „recycling technology“ or of luminescent materials.

This presentation will report new results acquired on lanthanide and alkali halide molten salt solutions from several physicochemical techniques. Examples will be given of systematic trends in the thermodynamic features and correlated to structural features.

Transport Properties of Imidazolium-Based Ionic Liquids at High Pressures

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The pressure dependences of the ionic diffusion coefficients and the viscosity of two imidazolium-based ionic liquids have been determined at pressures up to 200 MPa.

Their behaviour is qualitatively different from that of molecular liquids, with isotherms being best fitted as functions of the applied pressure rather than as functions of the molar volume. Modified Litovitz and Vogel-Fulcher-Tammann equations have been used to incorporate both the temperature and pressure dependence. For the viscosity, the T_0 parameter of the VFT equation appears to be independent of pressure within the state point range of the data: consequently the fragility factor is pressure dependent, increasing with increasing pressure.

Structures of 1-Butyl-3-Methyl-Imidazolium Hexafluorophosphate Ionic Liquid and Its Carbon Dioxide Solutions

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In order to develop environmentally-benign chemical processes, we have studied fundamental solvent properties of supercritical fluids[1] and room-temperature ionic liquids[2] by means of spectroscopic and conductometic techniques. In the present work, we investigate liquid structures of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and its carbon dioxide solutions on the basis of neutron and X-ray diffraction experiments.

Neutron diffraction measurements were performed at 25 ^{O}C using the HIT-II spectrometer in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The H/D isotopic substitution technique was applied to hydrogen atoms in the imidazolium ring of $[BMIM]^+$ so as to determine the liquid structure around the anisotropic cation. The scattered intensities were collected for five samples of (I) 2,4,5-D(98%)-[BMIM][PF_6], (II) 2-D(98%)-4,5-H-[BMIM][PF_6], (III) 2-H-4,5-D(98%)-[BMIM][PF_6], (IV) 2-D(98%)-4,5-D(49%)-[BMIM][PF_6], and (V) 2-D(49%)-4,5-D(98%)-[BMIM][PF_6]. The first-order difference function for each set of combination in terms of 2-H (I-III and I-V) and 4,5-H (I-II and I-IV) was derived from the numerical difference between the observed scattering cross sections. Then, we determined the partial structure factors and the distribution functions relating with the 2-H and 4,5-H atoms. The observed partial structure factors were analyzed by the lease squares fitting procedure. The nearest neighbour 2-H...2-H and 4,5-H...4,5-H distances were 3.40(2) and 3.80(2) Å with the coordination numbers being 0.89(4) and 0.92(3), respectively.

X-ray diffraction measurements were carried out at 25 ^{O}C for three samples of neat [BMIM][PF_6] and [BMIM][PF_6] solutions saturated with CO_2 at 4 and 13 MPa. The molar ratios (x) of CO_2 in the three samples were 0, 0.5, and 0.7, respectively, according to the solubility data.[3] The intramolecular contribution of [BMIM][PF_6] was calculated from the structural data of the cation[4] and the anion[5] species. The intermolecular distribution function, $g^{\text{inter}}(r)$, was determined by the Fourier transform of the intermolecular interference term, which was obtained by subtracting the intramolecular interference contribution from the total interference term. In the $g^{\text{inter}}(r)$ of the sample with $x = 0.5$, two peaks appeared at around 2.8 and 3.2 Å. These two peaks appreciably increased in $x = 0.7$; moreover, there was another peak observed at ~3.8 Å. The results of the least squares refinement strongly suggest that CO_2 molecules are preferentially solvated to the PF_6^- anion. The nearest neighbour $P(PF_6)$...$C(CO_2)$ distances were 3.57(1) and 3.59(1) Å with the coordination numbers being 1.8(1) and 4.0(1) for $x = 0.5$ and 0.7, respectively.

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Ionic Liquids as Solvents in Separating Organic Liquid Mixtures

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Ionic Liquids offer a new and exciting range of solvents for both extractive distillation and solvent extraction processes for separating organic liquid mixtures. In this work a number of ionic liquids are used to investigate the separation of organic liquid mixtures such as aromatic compounds from aliphatic compounds. The ionic liquids include: $[HMIM]^+ BF_4^-$, $[HMIM]^+ PF_6^-$, $[BMIM]^+ PF_6^-$, $[OMIM]^+ Cl^-$, $[BMPY]^+ BF_4^-$, $[EMIM]^+ I_3^-$, $[BMIM]^+ I_3^-$, $[EMIM]^+ C_8H_{17}SO_4^-$, $[BMIM]^+ CH_3(OC_2H_4)_2SO_4^-$ and a phosphonium ionic liquid trihexyl-tetradecyl phosphonium chloride or tris(pentafluoroethyl)trifluorophosphate.

The tie-lines of ternary phase diagrams are used to determine the Selectivity of each ionic liquid for a particular separation process and the efficacy of each ionic liquid is then predicted. Although these Selectivity values are important they must be looked at with other phase diagram properties in mind, such as the magnitude of the partially miscible region and their solubility, when considering commercial separation.

The ternary phase diagrams are dependent on the mutual solubilities of the three components involved. These solubilities can be used to predict crude phase diagrams and tie-line data for any ionic liquid + organic liquid mixtures. The phase equilibria and solubility data, discussed in this work, have been obtained in the authors' laboratory and from data reported in the literature.

The results in this work have also been extrapolated to predict the molecular structures of potentially more effective ionic liquids for the separation processes discussed here.

These Selectivities also have a bearing on the efficacy of ionic liquids in separating liquids using extractive distillation.

Activity coefficients at infinite dilution of organic liquid solutes in Ionic Liquid solvents have also been measured in order to predict the possibility of using these Ionic Liquids as solvents in extractive distillation processes. The results of our work and those of other workers are discussed in this work and related to the conclusions obtained from the phase equilibria work.

DFT Calculations and Raman Spectroscopic Study on the Solvent Conformation Change upon Coordination to Metal Ions

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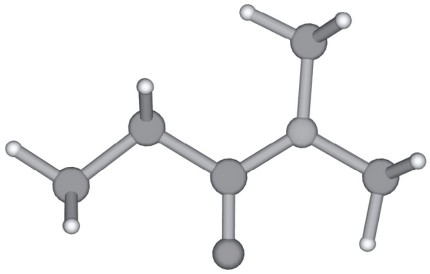
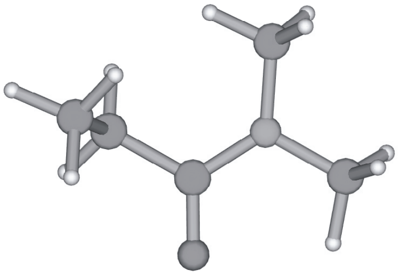
It is necessary to elucidate metal ion solvation structure at a molecular level in order to understand its reaction in solution. In the bulky aprotic donor solvents such as 1,1,3,3-tetramethylurea (TMU), Hexamethylphosphoric triamide (HMPA), the steric interaction in the first solvation shell around the metal ion plays a key role, *i.e*. the steric hindrance among solvent molecules in the first solvation shell decrease a metal ion solvation number, which strongly enhance its complex formation with halide ion.

In this aspect, solvent molecules have been considered to be rigid and their molecular structural change could be negligible. *Is this a true?* Recently, we found that *N*,*N*-dimethylpropionamide (DMPA) changes its molecular structure when it solvates to relatively small metal ions such as Mn^{2+}, Zn^{2+} and Mg^{2+}. This is *Coordination Change upon Coordination to Metal ion*, *CCCM*. We also demonstrated that *CCCM* could be decisive factor whether metal ion harogeno complex formation was exothermic or endothermic. With regard to Mn^{2+}, monobromo complex formations are endothermic in DMPA and exothermic in TMU, respectively, although Mn^{2+} is five-coordinated structure in both solvents. It is evidently that *CCCM* more stabilize Mn^{2+} in DMPA.

In order to discuss more detail *CCCM*, density functional theory (DFT) calculations were carried out. Potential energy surfaces as a function of O-C-C-C torsion angle with and without metal ion and DMPA conformation in the first solvation shell around the metal ion will be discussed.



planar cis



nonplanar staggered DMPA

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Liquid-Liquid Equilibria, Liquid Densities and Interphase Tension Measurements in Ionic Liquid + Non-Aqueous Solvent Mixtures

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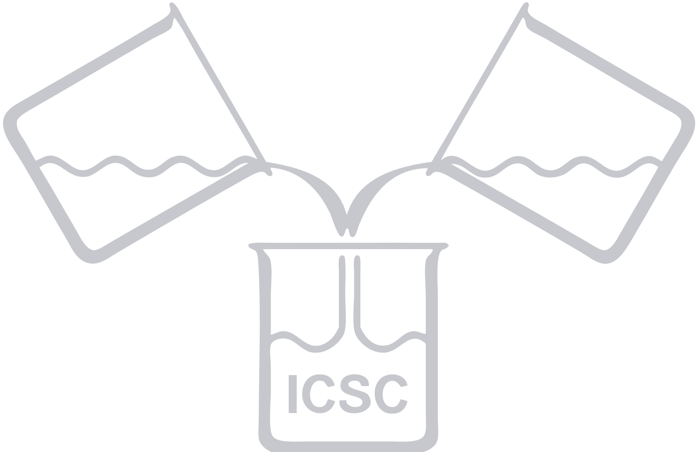
Experimental results of the thermodynamic coexistence curve for liquid-liquid phase equilibria of binary mixtures containing the ILs [C_4MIM][NTf_2], [C_6MIM][NTf_2], or [C_8MIM][NTf_2] mixed with different alcohols (propan-1-ol, butan-1-ol, pentan-1-ol, cyclohexanol, or hexan-1,2-diol) are reported. The results have been obtained using a laser light scattering method which allows to detect demixing temperatures as function of the liquid composition with high precision even in cases where only small liquid samples are available. In some cases quantitative UV-VIS light absorption technique has also been applied as supplementary method to determine liquid-liquid two phase coexisting lines. In all binary systems upper critical solution temperatures (UCST) have been found.

For some of these binary systems densities and excess volumes have been measured using the technique of the vibrating tube. It is shown that corrections due to the large difference in viscosities of the pure liquids and the mixtures have to be accounted in order to obtain densities with reliable precision.

The interphase tension between liquid phases in IL mixtures is of a great interest for dealing with the problem of generating droplet small enough to support effectively interphase catalytic processes taking place in biphasic mixtures containing ionic liquids. An experimental set up using the technique of the pendant drop will be presented and some results of interphase tension data of the liquid-liquid system ([C_4MIM][NTf_2] + butan-1-ol) are reported.

F.
SOLVENTS AND SOLUTIONS UNDER EXTREME CONDITIONS

Poster Presentations



Spectroscopic Studies of Sulfite Species

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Sulfur K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy has been used to study aqueous sulfite solutions at different pH. The shape and position of the features in the x-ray absorption spectrum reflect the influence on the energy levels by the oxidation state and the chemical surrounding of the sulfur atom, making the sulfur XANES technique very useful for this spectroscopically “silent” element. Detailed interpretation of the spectra is possible by theoretical computation of the transition energy of the sulfur 1s electron to unoccupied states of 3p character by means of the Density Functional Theory – Transition Potential method (DFT - TP). This has allowed simulation of the position and splitting of the peaks in the experimental XANES spectrum of the SO_2 molecule and confirms that the hydrated sulfur dioxide molecule, $SO_2(aq)$, is the dominating species in sulfite solution at low pH (<2). In the intermediate pH range, $2 < pH < 7$, the XANES spectra reveal the presence of both the isomeric species, HSO_3^- and SO_3H^-, the hydrogen sulfite and the sulfonate ions with the hydrogen atom coordinated to the sulfur and oxygen atoms, respectively. The SO_3H^- isomer is dominating but with increasing temperature the relative amount of the HSO_3^- isomer increases. The XANES spectrum of the methanesulfonate anion, $CH_3SO_3^-$, in aqueous solution was recorded for comparison to the HSO_3^- species, and their theoretically computed spectra exhibit similar features. However, the spectrum of the solid $CsHSO_3$ compound, comprising HSO_3^- and Cs^+ ions, differs from the spectrum in aqueous solution both regarding the absolute peak positions and the features exhibited. The so-called shape resonances due to the neighbours of the excitation site (the sulfur atom) in the solid $CsHSO_3$ compound give rise to multiple-scattering effects in the XANES spectra. Rietveld analysis of neutron powder diffraction data was used to determine the S - D bond distance in solid $CsDSO_3$, as preliminary to the computation of theoretical spectra. Also the bonding and force field was evaluated by normal coordinate analysis of the IR and Raman vibrational spectra of the HSO_3^- and DSO_3^- ions.

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Melting Point Depression by Using Supercritical CO_2 for a Novel Melt Dispersion Micronization Process

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Fine particles of active agents can be produced by a melt dispersion process: the solid particles are dispersed in a liquid and heated above their melting temperature. The emulsion is treated mechanically to produce fine droplets. Subsequently the emulsion is cooled down and a dispersion of fine solid particles is achieved. For many temperature sensitive substances, this process has the disadvantage that heating above the melting temperature causes degradation of the substance. In a novel process supercritical fluids are used to lower the process temperature by reducing the melting temperature of the dispersed active agent. It has been proven for several active agents that by dissolving a considerable amount of a supercritical fluid a reduction in the melting temperatures of 30 K – 50 K compared to the melting temperature of the pure active agent can be obtained.

In this work, the effect of carbon dioxide (CO_2) on the melting behavior of active agents and model substances was investigated. Different binary (solid substance – CO_2) and ternary (solid substance – CO_2 – water) systems were studied in a high pressure view cell. A large sapphire window (50 mm diameter) facilitated the observation of phase transition. Four different solid substances were tested: phenanthrene, beta-sitosterol, an insecticide and a pharmaceutical active. The experiments were performed at temperatures up to 508 K and at pressures up to 30 MPa. The various melting points for every material under different pressures were plotted on the temperature – pressure plane, thus forming the system's Solid-Liquid-Vapor (SLV) line. The results for phenanthrene, which was used as a model compound, were compared with similar measurements performed in a different high pressure apparatus. Good agreement was observed.

For the pressures tested in this work, the insecticide exhibited the largest melting point depression of 34.2 K (at 200.5 bar) in its binary system, and 69.4 K (203.7 bar) in its ternary system. Beta-sitosterol, the pharmaceutical active and phenanthrene under CO_2 pressure showed maximum melting point depression values of 34.2 K (138.0 bar), 16.9 K (274.8 bar) and 13.5 K (97.7 bar) respectively.

The material's specific behavior during the phase transition (form of the substance, degradation) and the eye of the experimentalist are two very significant factors because of the fact that the applied method was visual. Finally, the modeling of the data obtained was conducted with the help of a thermodynamic framework based on cubic equations of state.

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EuBr$_2$-KBr Molten Salt Solutions: Experimental and Numerical Investigations

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The present work, which is a part of a general research program on lanthanide halides and their mixtures with alkali metal halides, focus on the EuBr$_2$–KBr binary system. The phase diagram of as well as electrical conductivity of pure EuBr$_2$ and its mixtures with potassium bromide were investigated experimentally.

Differential Scanning Calorimetry was used to study phase equilibrium in this system. It exhibits two eutectics at 810 K and 852 K, respectively. It also includes two stoichiometric compounds, K_2EuBr_4, decomposing peritectically at 829 K, and KEu_2Br_5, melting congruently at 880 K.

Electrical conductivity measurements were performed complementarily Measurements were performed over the entire composition range by increments of ~ 10 mol%. The main goal was to investigate the conductance of the liquid phase. However, the solid phase was also examined at some compositions for the purpose of correlating the characteristic temperatures determined by DSC A quite good compatibility can be observed between the temperatures T_{dec} (K_2EuBr_4) and T_{fus} (KEu_2Br_5) determined from the two techniques.

Heat capacity measurement were also performed on the compounds.

Finally the CALPHAD method was used to critically evaluate the whole experimental data and to establish numerically phase equilibria from the optimized thermodynamic properties.

Kinetics of Vegetable Oil Alcoholysis under Methanol Supercritical Conditions

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Methanol under supercritical conditions has a large kinetic energy which is similar to the kinetic energy of gases and its density is close to the density of liquid methanol. This is one of reasons for increase the rate of vegetable oil alcoholysis under such conditions, caused also by drastical change of metahnol dielectric constants, from 32 (normal conditions) to 7 (239 ºC and 8.09 MPa). Such dielectric behaviour of supercritical methanol is similar to the typical dielectric characteristics of non-polar organic solvents. Obviously that condition, necessary for making the pseudo-homogeneous phase system (vegetable oil and methanol), exists under supercritical conditions, thus favoring the reaction rate of supercritical alcoholysis.

Alcoholysis of vegetable oil is very complex process, formally defined by combination of three reversible and series-parallel reactions. The formal rates of such complex reaction scheme, assuming that easch step is also elementary, could be defined by the following expression:

$$\mathrm{TG + MeOH \leftrightarrow DG + FAME} \qquad r_{1,F} = k_{TG}C_{TG}C_M - k'_{TG}C_{DG}C_F$$
$$\mathrm{DG + MeOH \leftrightarrow MG + FAME} \qquad r_{2,F} = k_{DG}C_{DG}C_M - k'_{MG}C_{MG}C_F$$
$$\mathrm{MG + MeOH \leftrightarrow GL + FAME} \qquad r_{3,F} = k_{MG}C_{MG}C_M - k'_{G}C_{G}C_F$$

where: k_{TG}, k_{DG} and k_{MG} are the reaction rate constants for the fatty acid methyl ester (FAME) formations in easch of three reactions; k'_{TG}, k'_{DG} and k'_{MG} are the corresponding reversible reaction rate constants; and, C_{TG}, $C_{DG,}$ $C_{MG,}$ C_M, C_G, and C_F are concentrations of tri-, di- and monoglycerides, methanol, glycerol and FAME, respectively. Because a large excess of methanol is usually applied for supercritical alcoholysis (SCA), the preliminary analysis of kinetic data showed that reversible reactions are not important.
Kinetics of triglicerides alcoholysis is the most important parameter for proper design of technological scheme of FAME (biodiesel) production under supercritical conditions. The analysis of such kinetic expression by use recently published data in literature as well as those performed with animal (pork) fat, used and virgin vegetable (sunflower) oil in this study, indicated drastical change of reaction rate constants (activation energy and frequency factor) if operating conditions of alcoholysis was changed from subcritical to supercritical. Such effect of pressure and temperature on reaction rate constant(s) were related to the change of methanol density under supercritical condition.

High-Pressure NMR Studies on Fluids Confined in Nanopore

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The properties of fluids confined in nanopore have attracted much interest in fundamental science, while they are also important in applications. Drastic changes of the phase behaviors of confined fluids,[1] such as the lower shift of the critical temperature,[2] are observed.

In the present study, high-pressure NMR spectroscopy was applied to fluids confined in nanopore. A 10mm-PEEK polymer tube with a Ti head plug was used as the sample cell. Xe or SF_6 gas was compressed by a syringe pump into the sample cell, where porous Vycor glass was partially filled. The ^{129}Xe- or ^{19}F-NMR spectra were measured by a spectrometer (Varian Inova 500) up to 340 K and 16 MPa.

Two distinct signals due to bulk and confined fluids are observed in a wide range of density from the gas phase to the liquid phase including the supercritical region. In Fig. 1, the ^{129}Xe-NMR chemical shifts of bulk and confined Xe are plotted as a function of pressure. While the chemical shift of bulk Xe is simply explained by bulk density, the chemical shift of confined Xe shows rather complicated behavior. Below the pore critical temperature (~250K,[2] hysteresis loops are observed; the chemical shift shows a rapid increase at compression, and a gradual decrease followed by a jump at decompression. These loops are explained by matastable states due to the evaporation or the condensation of confined Xe.[3] In Fig. 2, the mean density in nanopore, which is estimated from the ratio of the integrated signal intensities of bulk and confined SF_6, is plotted against bulk density. The correlation of the mean density in nanopore with the chemical shift and the longitudinal relaxation time is discussed at the presentation.

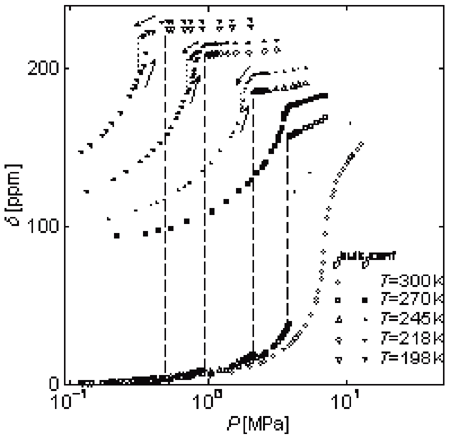

Fig. Pressure dependence of chemical shifts for Xe (open symbols) and confined Xe (closed symbols).

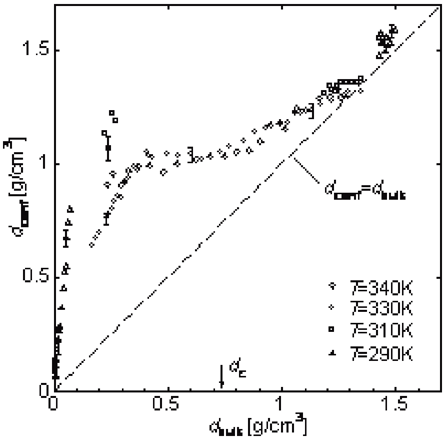

Fig.2 Mean density d_{conf} in nanopore as abulk function of bulk density d_{bulk} for SF_6

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Magneto-Structural Characterization of a Helical Polymeric Chain

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Following our interest in the stereochemistry of nitronyl nitroxides and their coordination complexes, we report here the spontaneous resolution and absolute configuration of conformational enantiomers of a coordination polymer comprising of a ferrocenyl bis(nitronyl nitroxide) and manganese(II) bis(hexafluoroacetylacetonate). The compound is intriguing in the sense that there are seven interrelated sources of conformational chirality in the system, which presumably propagate along the chain during its formation and manifest themselves macroscopically in the form of two enantiomorphic crystals.

The complex shows a remarkable structure which resolves spontaneously upon crystallization revealing seven sources of chirality, which are probably determined ultimately by the configuration of the manganese(II) ion. However, in order to take advantage of the optical activity in the present case the tedious separation procedure of the enantiomorphs described above has to be undertaken.

Acknowledgment. This work was supported by grants from the Programa Nacional de Materiales of the DGI (Spain), under project MAT2000-01388, Acción Integrada Hispano-Austríaca (HU-1999-0015), the ESF Molecular Magnetism Network, the 3MD Network of the TMR program of the EU (contract ERBFMRX CT980181), and the FWF Vienna (P13128).

Computer Simulation Investigation of the Water-Benzene Interface in a Broad Range of Thermodynamic States from Ambient to Supercritical Conditions

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The dependence of the properties of the water-benzene system on the thermodynamic conditions in a broad range of temperatures and pressures has been investigated by computer simulation methods. For this purpose, simulations have been performed at 23 different thermodynamic states, ranging from ambient to supercritical conditions. The density profiles of the water and benzene molecules have been determined at each of the thermodynamic states investigated. Information on the dependence of the mutual solubility of the two components as well as of the width of the interface on T and p has been extracted from these profiles. The width of the interface has been found to increase with increasing temperature up to a certain point, where it diverges. The temperature of this divergence corresponds to the mixing of the two phases. The determination of the critical mixing temperature at various pressures allowed us to estimate the upper critical curve, separating the two-phase and one-phase liquid systems, of the phase diagram of the simulated water-benzene system.

In analyzing the preferential orientation of the molecules relative to the interface it is found that the benzene molecules prefer to lay parallel with the interface, the water molecules penetrated deepest into the benzene phase prefer to stay perpendicular to it pointing by an O-H bond almost straight toward the benzene phase, whereas the waters located at the aqueous side of the interface are preferentially aligned parallel with the interfacial. Although the strength of the orientational preferences decreases rapidly with increasing T, the preferred orientations are found to be independent from the thermodynamic conditions. The analysis of the relative orientation of the neighboring water-benzene pairs has revealed that the radius of the first hydration shell of the benzene molecules is independent from the thermodynamic conditions, even if the system consists of one single phase. It has been found that the nearest water neighbors of the benzene molecules are preferentially located above and below the benzene ring, whereas more distant water neighbors, belonging still to the first hydration shell, prefer to stay within the plane of the benzene molecule. In the two-phase systems the dipole vector of the first hydration shell waters has been found to be preferentially perpendicular to the vector pointing from the center of the benzene molecule to the water O atom.

Studying Thermodynamic Properties of Liquid Alkali-Metal Mutual Solutions with Application of the Effusion Method New Variant in the Pressure Range Between Knudsen's and Hydrodynamic Efflix Models

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Direct measurement of thermodynamic activity of components a_i for the liquid metal mutual solutions at high temperatures is extremely difficult with respect to alkali metals. The reasons are the absence of stable high-temperature solid electrolytes with the required ion composition to be used for concentration cell membranes (for EMF method), the interferation of radiation of the respective lines (for the atomic absorption method) and too high saturation pressure (for effusion method). Therefore instead of direct measurement of component activity of the liquid alkali metal mutual solution at high temperatures, use is made of the calculation-experimental method based on determination of this function within a wide range of temperatures T and concentrations x_i through integration of the differential equation of chemical thermodynamics:
the solution of which has a form:

$$\left[\partial \ln a_i / \partial(1/T)\right]_{p,x_i} = \Delta\overline{H}_i / R \qquad (1)$$

where the integrand $\Delta H_i(T, x_i)$, i.e. the partial enthalpy of formation within the entire ln $a_i = f(T_1, x_i)$ region

$$\ln a_i(T, x_i) = \ln a_i(T_1, x_i) - R^{-1}\int_{T_1}^{T} \Delta\overline{H}_i(T, x_i)T^{-2}dT \qquad (2)$$

of parameters under the study ($400 \le T \le 1200$K, $0 \le x_i \le 1$), as well as boundary condition , i.e. the concentration dependence of component activity only at one not high reference temperature T_1 ($400 \le T_1 \le 450$K) within the entire range of x_i, are determining in the experiment. Thus the algorithm of the research allows determining thermodynamic activity at high temperatures without resorting to its direct measurements in this area. This method does not require any special assumptions and can be furnished with reliable input experimental data.

The object of this work is developing the method and measuring the activity (Gibbs energy) on the reference isotherm T_1 for determining the boundary conditions ln $a_i = f(T_1, x_i)$ when integrating (1), what enables to close the thermodynamic description for the alkali-metal binary and ternary mutual solutions (Cs-Na, K-Na, Cs-K, Cs-K-Na) in all above range of parameters under the study. This activity was determined using the components partial pressures. It was done by the effusive method with measurement of atomic beam intensity. The pressure range in these experiments was intermediate between Knudsen's mode and hydrodynamic one. A detailed analysis shows that it is possible to operate outside the range where the Hertz-Knudsen equation applies. As oxygen inevitably reacts with a molten alkali metal, the effusion hole cannot be made in advance. Therefore, the effusive hole was machined directly in the vacuum chamber by the electron-ray pulse (the electron linear accelerator was located inside the chamber) after the cell acquired the working temperature T_1.

The Structure of Liquid Antimony Pentafluoride

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Antimony pentafluoride, SbF_5, is an archetype for associated fluids that are bound by **3 c**enter – **4 e**lectron (3c-4e) interactions that are not hydrogen bonds where the most important chemical feature of SbF5 is its ability to act as a fluoride ion acceptor. The structure of SbF_5 in the solid state shows a high degree of association and consists of molecular, tetrameric of SbF_5 with a density of 4.07 g cm^{-3}.[1] However in the liquid state, the density is 3.16 g cm^{-3} at 281.65 K this large change in density between the two states, ~22%, is indicative of a large structural change in the fluid.[2] The structure of liquid SbF_5 has been investigated using neutron high energy X-ray diffraction. The resultant diffraction data was modelled using the disordered materials program **E**mpirical **P**otential **S**tructure **R**efinement (EPSR). The results show that SbF5 is highly associated in the liquid phase and forms a range of possible polymeric structures.

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Multi Step Electrochemical Reactions of Niobium Metal Surface in KOH Solutions

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The multi step electrochemical reactions of niobium metal surface, in various concentrations of KOH aqueous solutions, were studied at open circuit potentials and during the electrochemical polarization. The potential time profiles at open circuit potential reveal that in lower concentrations of KOH the small thickening of natural oxide film on Nb surface occurs. In higher concentrations this film is sinking under continuous dissolution. The I-E profiles of potentiodynamic measurements reveal to the active/passive transition of the metal electrode and big influence of the KOH concentration to the processses of reactivation. The passive film of cathodically pre-treated Nb electrode consists four various oxides with thermodynamically most probable composition of: NbO, NbO_2, Nb_2O_5 and $Nb_2O_5 \cdot H_2O$,[1] Fig. 1. The degree of the progress of each reaction depends of the concentration of KOH, surface pre-treatment and initial electrochemical conditions.

The effects caused by increasing KOH concentrations can be interpreted on the basis of enhanced solubility of Nb oxides. Inspection of the data recorded for all investigated concentrations reveals that two different mechanisms: the electrochemical passivation and dissolution of passive film occurring on electrode surface

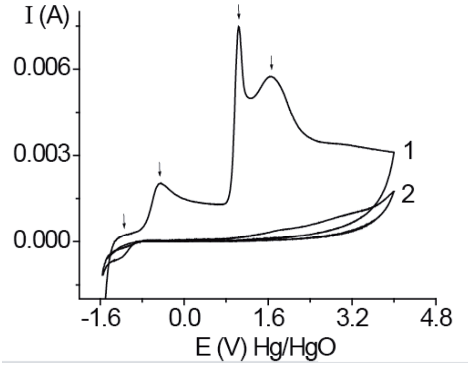

Fig.1. 1-th and 2-nd cycle recorded on Nb in 2 M KOH (v = 100 mV/s)

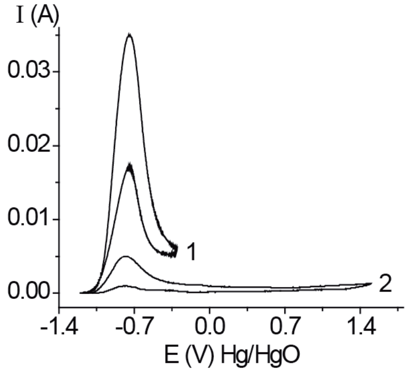

Fig.2. 1-st and 2-nd cycle recorded on Nb in 10 M KOH (v = 100 mV/s)

These two mechanisms could be seen on Fig. 2., where the reactivation process significantly participated in the passivation process. The calculated values of anodization coefficient α (nm/V) increased with increasing the concentration of KOH (from 15 nmV in 0.1 M KOH to 40 nm/V in 10M KOH).

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Low Temperature Raman Scattering Investigation of the Crystal α and β of Acetonitrile. Premelting Structure-Crystallization and Glass Formation Processes in Methylcyclohexane. Vibrational Dynamics as a Possible Molecular Indicator of the Phase Transitions.

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Vibrational dynamics of the internal modes combined with the low frequency phonon Raman spectra studied by the Raman spectroscopy in the broad temperature range (298 K-10 K) are powerful indicators to specify phases and phase transitions at the molecular level.
We have specified the nature of the correlation between the liquid-solid β and solid β-solid α transitions of acetonitrile by Raman spectroscopy for the first time.

All the vibrational modes of acetonitrile are very sensitive to the structural changes that occur at the liquid-β solid at 229 K and β solid -α solid at around 208-212 K. Key characteristics of the molecular dynamics leading to structural reorganization at both phase transitions is that they involve reorientational or librational motions around the axis perpendicular to the C_3 molecular axis. The β-α transition in acetonitrile is accompanied by a drastic change in the orientation of the molecular dipole moments from an antiparallel alignment for the neighboring molecules in the β phase to a parallel alignment in the α phase. Such a large angle reorientation of acetonitrile molecule is possible in the β phase where the crystal structure is not fully formed and it exhibits a large degree of plasticity.[1]

The results of Raman studies on vibrational dynamics and static properties of the CH_2 rocking mode of methylcyclohexane (MCH) as a function of temperature and cooling rate in the range 298 K-10 K have identified for the first time the premelting structure (crystal β) of MCH in the range 140-147 K that proceed the melting both for the glassy state and the equilibrium crystal state (crystal α) of MCH.

It was found that MCH in the undercooled liquid phase may form distinct thermodynamic states that strongly depend on the quenching rate. We have identified the characteristic temperature T^* that is quenching rate dependent which is the no-return-point between crystallization and amorfization.[2,3] Below this temperature the undercooled methylcyclohexane exists in either the liquid state that is out of equilibrium and represents nonergodic behavior that leads to glass forming or in the metastable equilibrium ergodic state that leads to crystallization. Deuterated MCH exists only in one crystal form within the studied temperature range.

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On the Conformation of *Room Temperature Ionic Liquid* 1-Methyl-3-Ethyl-Imidazolium Cation

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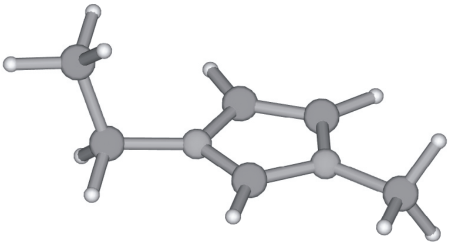
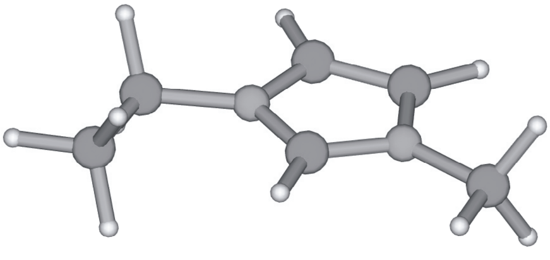
Raman spectra at the frequency range of 200 – 1600 cm^{-1} of Room Temperature Ionic Liquids, 1-ethyl 3-methyl imidazolium salts (EMIX, X : tetrafluoroborate, BF_4^-, hexafluorophosphate, PF_6^-, trifluoromethanesulfonate, $CF_3SO_3^-$, and bis- (trifluoromethanesulfonyl) imide, TFSI) were measured at room temperature for BF_4^-, triflate and TFSI salts and at slightly above its melting point for PF_6^- salt. Raman spectra for $EMIBF_4$ and $EMICF_3SO_3$ with varying temperature were also measured. DFT and *ab initio* calculations of the isolated EMI cation in gas phase were performed.

Raman spectra except those of anions were well explained by theoretical calculations for the well recognized *no planar* EMI cation in gas phase. Observed Raman band at 448 cm^{-1}, however, could not be explained in terms of the *non planar* EMI cation. Torsion energy profiles of an ethyl group in EMI cation were thus calculated by HF, B3LYP and MP2 levels of theory using 6-311+G(d,p) and aug-cc-pvDZ basis sets. Two local minima were found in the torsion energy profile around N-C(methylene carbon in an ethyl group of EMI) bond, *i.e.* the *non planar* and *planar* isomer, in which an ethyl group locates on the imidazolium plane. Full geometry optimizations followed by normal frequency analyses for the two isomers were performed and confirmed that the well recognized *non planar* isomer is the grovel minimum, and that the *planar* isomer is also stable (not saddle point) and exists as about 2 kJ mol^{-1} higher local minimum.

Theoretical Raman spectra for the *planar* isomer were also obtained, which well explains the observed Raman band at 448 cm^{-1}. The conformational isomerization enthalpies $\mathbf{\Delta}_{\mathrm{iso}}H°$ from *non planar* to *planar* isomer were evaluated by temperature dependence of Raman spectra to be 3 kJ mol^{-1} and 2 kJ mol^{-1} for BF_4^- and triflate salts, respectively. We thus propose that EMI cation exists in a conformational equilibrium at examined temperatures



non planar EMI



planar EMI

Heterogenization of Supercritical Fluids in Ternary Water-Salt Systems

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Supercritical fluid (SCF) equilibria (where the fluid is homogeneous at any pressure) in some binary systems with volatile and nonvolatile components (in particular, in the water-salt systems) take place not only at temperatures above the critical points of both components but also at lower temperatures. Such "low-temperature" SCF equilibria arise as a result of critical phenomena in solid saturated solutions (critical endpoints p and Q) in the systems of type 2, where the melting temperature of nonvolatile component is above the critical temperature of volatile one, and take place in the temperature range between points p and Q. In the case of binary systems of type 1, the melting temperature of nonvolatile component can be above or below the critical temperature of volatile one, and the "low-temperature" SCF equilibria are absent.

If the binary subsystems with components of different volatility in the ternary system belong to the different types (types 1 and 2), the "low-temperature" SCF equilibria spreading from the binary subsystem of type 2 should transform (as a result of heterogenization of the homogeneous SC fluid) into liquid-gas equilibria that are typical for the binary system of type 1.

The experimental studies (at temperatures up to 500 ^{o}C and pressures up to 150 MPa) of ternary systems K_2CO_3 – Na_2CO_3 – H_2O and KCl – K_2SO_4 – H_2O (where the binary subsystems K_2CO_3 – H_2O and KCl – H_2O belong to type 1, and Na_2CO_3 – H_2O and K_2SO_4 – H_2O belong to type 2) show two versions of a heterogenization process for the SC fluid. A separation of the three-component homogeneous fluid saturated with a salt into two solutions occurs as a result of critical phenomena taking place along the critical curves starting in the nonvariant critical points p and Q of type 2 binary subsystem. Most likely these two critical curves in the system K_2CO_3 – Na_2CO_3 – H_2O are joined in one monovariant critical curve pQ with a maximum content of K_2CO_3 in the double critical endpoint. In the case of the system KCl – K_2SO_4 – H_2O, the critical curves starting in the points p (g=l-s_{K2SO4}) and Q (l_1=l_2-s_{K2SO4}) are directed on to high temperature but do not join. They end in the ternary nonvariant critical points pR (l_1=g-l_2-s_{K2SO4}) and QN (l_1=l_2-g-s_{K2SO4}), which terminate the four-phase immiscibility region l_1-l_2-g-s_{K2SO4}. The monovariant critical curves with equilibria l_1=g-l_2 and l_1=l_2-g start from the points pR and QN toward high temperatures and intersect in the tricritical point RN (l_1=l_2=g).

The most outstanding distinction of these ternary systems which can give rise the mentioned features of phase behavior is the fact that the binary subsystem of type 1 (K_2CO_3 – H_2O) is complicated by the immiscibility phenomena, whereas another ternary system contains the binary subsystem of type 1 (KCl – H_2O) without the immiscibility equilibria.

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Inorganic reagents

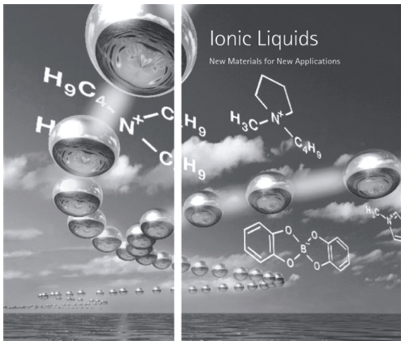
-acids and salts
-caustic alkalies and lyes
-buffers
-volumetry
-standards
-Karl Fischer reagents

Solvents

-HPLC (LiChrosolv/Prepsolv)
-GC (SupraSolv/UniSolv)
-extractions (GR-Grade)
-spectroscopy (Uvasol)
-preparative laboratory work (For Synthesis)
-production (Extra pure)
-DNA synthesis (SeccoSolv dried)

Ionic liquids

New generation materials



Microbiology

-culture media

Chromatography

-HPLC columns and accessories
-preparative chromatography
-thin layer chromatography
-sample preparation

Hygiene monitoring

-HY-RISE – set for rapid surface cleanliness determination
-Envirocheck Contact Plates – for detection of microorganisms on working surfaces
-Envirocheck Dip Slides and Contact Slides – detection of microorganisms in fluids
-Readycult Coliforms and Readycult Enterococci – systems for determination of microorganisms in water

Food & Enviromental analysis

-Merckoquant, Aquaquant, Aquamerck and Microquant (quick visual tests)
-Spectroquant – quantitative spectrophotometric determinations
-Reflectoquant – reflectometric quantitative determinations
-Turbiquant – quantitative determination of turbidity


2000 ml
PYREX MADE U.S.A.
250 ml
KIMAX
1000 ml
KIMAX
U.S.A.
900 ml
800
700
600
500
100