CONFERENCE SERIES

Bernd M. Rode, Bernhard R. Randolf (Eds.)

31st International Conference on Solution Chemistry

Innsbruck / Austria
August 21 - 25, 2009

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Toshio Yamaguchi

31st International Conference on Solution Chemistry

Innsbruck, Austria August 21-25, 2009

Programme

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Austria

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Friday, 21-08-2009

Session 1: Chairman Ingmar Persson
09:30 – 10:00 Bernd M. Rode
Opening
10:00 – 11:00 Kurt Wüthrich
Solution NMR structures of Proteins - from Structural Biology to Structural Genomics

11:00 – 11:30 Coffee Break

11:30 – 11:50 Toshio Yamaguchi
Structure and Dynamics of Low Temperature Confined Water
11:50 – 12:10 Kavosh Majlesi
Application of Kamlet-Taft Equation for Determination of Solvatochromic Parameters in Mo(VI) + EDDA Complex
12:10 – 12:30 Nuryono
Adsorption of calcium(II), lead(II) and silver(I) on sulfonato-silica hybrid prepared from rice hull ash

12:30 – 14:30 Lunchtime

Session 2: Chairman Glenn Hefter
14:30 – 15:30 Susumu Kitagawa
Chemistry of Porous Coordination Polymers
15:30 – 16:00 Othmar Steinhauser
Relaxation of hydration shells in aqueous solutions of oligosaccharides, peptides and proteins
16:00 – 16:20 Evgenyi Shalaev
Medium effects in chemical instability of amorphous pharmaceutical systems

16:20 – 16:50 Coffee Break

Session 3: Chairman Alfred Laubereau
16:50 – 17:10 Klemen Bohinc
Interaction between charged surfaces induced by rod-like nanoparticles
17:10 – 17:30 Earle Waghorn
Hydrogen Bonding to Nucleic Acid Bases
17:30 – 17:50 Maria Clara Magalhães
Acid mine drainage (AMD) elemental total concentration reduction by biological apatites

18:30 – 20:00 Reception
Hosted by the Government of Tyrol and the City of Innsbruck

Saturday, 22-08-2009

Session 4: Chairman Bernd M. Rode

09:00 – 10:00 Sotiris Xantheas
An ab-initio based transferable interaction potential for water: Simulations of water clusters, liquid water, ice & hydrate networks

10:00 – 10:30 Enrique Sanchez Marcos
Solving the Hydration Structure of Metal Ions in Solution by Coupling MD simulations and X-ray Absorption Spectroscopies

10:30 – 11:00 Coffee Break

Session 5: Chairman Vojko Vlachy

11:00 – 11:30 Thomas Hofer
Characterisation of non-spherically solvated ions via molecular simulations

11:30 – 11:50 Laszlo Turi
Hydrated Electrons in Clusters, on Interfaces, and in the Bulk

11:50 – 12:10 Ivo Nezbeda
A problem of molecular theories of solutions: Can we predict correctly the properties of water-alcohol mixtures by computer simulations?

12:10 – 12:30 Myroslav Holovko
Thermodynamics of hard-sphere fluids confined in random porous media studied by scaled particle theory and computer simulations

12:30 – 14:30 Lunchtime

Session 6: Chairman Sotiris Xantheas

14:30 – 15:00 Vojko Vlachy
Ionenes, hydrophobic polyelectrolytes with unusual solution thermodynamic properties

15:00 – 15:20 Jean-Francois Dufreche
Coarse-graining in electrolyte solutions: toward a simple but molecular description of ion specific effects

15:20 – 15:40 Harno Pranowo
Conformational Analysis of the Microsolvation of [Li+.(12C4)], [Na+.(15C5)] and [K+.(18C6)] Complexes: Ab Initio Molecular Orbital Studies

15:40 – 16:00 Gyorgy Hantal
Molecular Level Properties of the Water-Dichloromethane Liquid/Liquid Interface, as seen from a theoretical investigation

16:00 – 16:20 Supot Hannongbua
Source of Drug Resistance: From 2004 H5N1 to 2009 H1N1 Influenza Viruses

16:20 – 16:50 Coffee Break

16:50 – 18:30 Poster Session 1

Posters 100 -199

19:30 – 21:00 Concert

Michael Tschuggnall

Sunday, 23-08-2009

Session 7: Chairman Alan Soper
09:00 – 09:30 Alfred Laubereau
Electron detachment from anions in aqueous solutions studied by two and three pulse femtosecond spectroscopy
09:30 – 10:00 Huib Bakker
Femtosecond study of the reorientation of water in solutions of ions and hydrophobes
10:00 – 10:30 Istvan Fabian
Light Induced Multistep Redox Reactions: The Diode Array Spectrophotometer as a Photoreactor

10:30 – 11:00 Coffee Break

Session 8: Chairman Pierre Turq
11:00 – 11:20 Akihiro Wakisaka
Azeotropy of Alcohol-Water Binary Mixtures from the Viewpoint of Microscopic Structures
11:20 – 11:40 Yasuhiro Umebayashi
On the Molecular Origin of the Nano-Segregated Structure of Ionic Liquids
11:40 – 12:00 Takayoshi Kimura
Interaction of chiral compounds in polar and non polar solution at 298.15 K
12:00 – 12:20 Zadjia Atik
Isobaric Solubility and Liquid–Liquid Equilibrium Measurements of 2,2,2-Trifluoroethanol with Cyclohexane and 2-Propanol at T = (288.15, 298.15, 308.15) K

12:20 – 13:30 Lunchtime

13:30 Excursions

Excursion A: Hafelekar Mountain

Meeting Point: "KRISTALLFOYER" (at the registration desks)

Excursion B: Crystal Worlds of Swarovski & Silver mine Schwaz

Meeting Point: "CASINOFOYER" (right in front of the lecture hall Room Innsbruck)

Monday, 24-08-2009

Session 9: Chairman Yitzhak Marcus

09:00 – 10:00 Ingmar Persson
Hydrated Metal Ions in Aqueous Solution – How Regular are Their Structures

10:00 – 10:30 Alan Soper
Water the solvent: latest insights into its structure from diffraction experiments.

10:30 – 11:00 Coffee Break

Session 10: Chairman Shin-Ichi Ishiguro

11:00 – 11:30 Yitzhak Marcus
The effect of ions on the structure of water: structure-making and –breaking

11:30 – 11:50 Natalie Malikova
Dynamics of water and ions in clays - neutron scattering and microscopic simulation

11:50 – 12:10 Iradwikanari Waluyo
Density fluctuations and local structures in aqueous solutions from x-ray spectroscopy and x-ray scattering measurements

12:10 – 12:30 Natallia Torapava
Structure Determination of Hydrated and Hydrolyzed Thorium (IV) Ions in Solution

12:30 – 14:30 Lunchtime

Session 11: Chairman Istvan Fabian

14:30 – 15:00 Maciej Smiechowski
Vibrational spectroscopy of HDO as a probe of solute hydration - a survey of recent investigations

15:00 – 15:20 Amalendu Chandra
Kinetics of proton transfer in aqueous systems of varying dimensions

15:20 – 15:40 S. Theodore David
Studies on Ionic Conductance of Solution Complexes of Some 3d- Metal Ions

15:40 – 16:00 Yurii Puhovski
Molecular dynamics simulations of ethanol-carbon dioxide mixtures along the liquid - vapor coexistence curve

16:00 – 16:20 Kalimi Mworia
Organisation for the Prohibition of Chemical Weapons (OPCW)

16:20 – 16:50 Coffee Break

16:50 – 18:30 Poster Session 2

Posters 200 -299

18:30 Banquet

Tuesday, 25-08-2009

Session 12: Chairman Andreas Bernkop-Schnürch

09:00 – 09:30 Glenn Hefter
Chemical Speciation and Other Difficulties in Ionic Liquids

09:30 – 10:00 Shin-Ichi Ishiguro
Structure, Solvation and Acid-Base Property in Ionic Liquids

10:00 – 10:20 Isabelle Billard
First determination of successive complexation constants in a ionic liquid: The UO_2^{2+}/NO_3^- system in C_4-mimTf_2N as studied by UV-vis and chemometric methods

10:20 – 10:40 Andrey Lyashchenko
Static Dielectric Constant and Water Activity of Concentrated Electrolyte Solutions

10:40 – 11:10 Coffee Break

Session 13: Chairman Othmar Steinhauser

11:10 – 11:30 Wolffram Schröer
The Liquid-Liquid Phase Transition in Solutions of Ionic Liquids

11:30 – 11:50 Pierre Turq
Transport coefficients: a path to explorate colloidal and polyelectrolyte solutions

11:50 – 12:10 Kenta Fujii
Alkyl-chain dependence on the liquid structure of 1-Alkyl-3-methylimidazolium based room-temperature ionic liquids

12:10 – 12:30 Richard Buchner
Ion Association in Solutions of Imidazolium RTILs: Combining Conductivity Measurements and Dielectric Spectroscopy

12:30 – 14:30 Lunchtime

Session 14: Chairman Thomas Hofer

14:30 – 15:00 Andreas Bernkop-Schnürch
Oral Drug Delivery: How do chemical reactions in the gastrointestinal tract influence the therapeutic potential of drugs?

15:00 – 15:20 Wolfgang Wachter
How Co-Ions Influence the Dynamics of Ionic Microemulsions - A Dielectric Relaxation Study

15:20 – 15:40 Ryo Kanzaki
Thermodynamic Study on the Autoprotolysis in a Protic Ionic Liquid, Ethylammonium Nitrate, and Its Aqueous Mixtures

15:40 – 16:00 Pierre Turq
Presentation of ICSC-32

16:00 – 16:30 Bernd M. Rode
Best Poster Award
Closing

Suggestions for Lunchtime-Meals

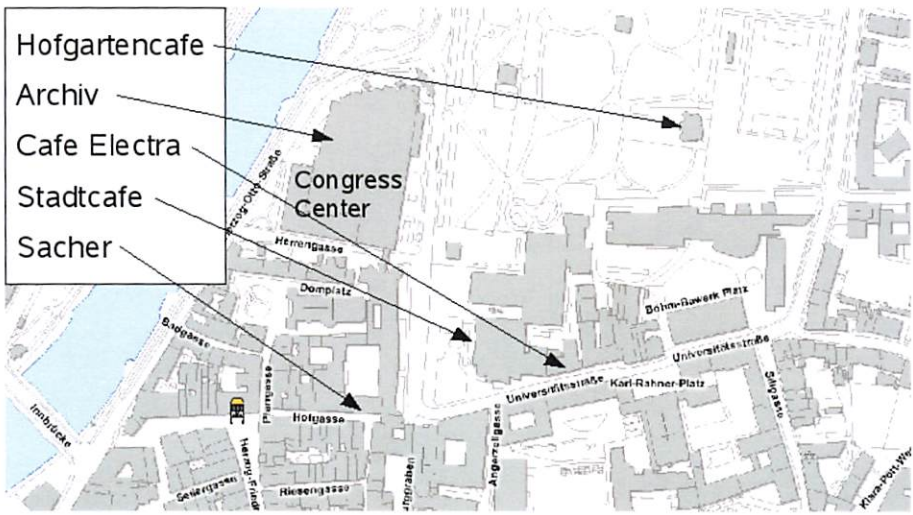
Café Sacher Innsbruck
Rennweg 1
Traditional, slightly up-priced cafe and restaurant, traditional Austrian cuisine including the famous Sachertorte. Outside Terrace.

Cafe Electra – Griechisches Kulturinstitut
Universitätsstrasse 3
The best greek restaurant in town.

Das Stadtcafé
Universitätsstraße 1
Contemporary cuisine,lunch-time menue for around € 8,-- Outdoor sitting,just opposite the Congress-House

Das Hofgartencafé u. Restaurant
Rennweg 6a
Across the road, through the park and sitting in a lovely shady beergarden, food is excellent and varied.

Archiv
Congress-House
Restaurant situated within the Congress-House
1 Menu (Meat or Vegetarian) € 7,50



31 st International Conference on Solution Chemistry

Innsbruck, Austria August 21-25, 2009

ICSC CONFERENCE CONCERT 2009

'Harmonic Oscillations between Classics and Pop'

MICHAEL TSCHUGGNALL

AUGUST 22, 19.30

Programme

Europe
Mozart, Sonata C major
Tears of Happiness
Liszt, Dreams of Love
Phoenix
Beethoven, Sonata C Sharp Minor
Eternity
Bach, Fuga C minor
From the East
Greek Intermezzo
Schrödinger's Equation

Michael Tschuggnall is a Master student of computer science at the University of Innsbruck and the winner of Austria's first 'Starmania' pop music contest. He composes all of his songs himself, but he is also educated as a classical pianist and music teacher

CONFERENCE SERIES

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Shimadzu
Tourismusverband Innsbruck

Welcome Address by Prof. Dr. Ingmar Persson
Chairman of the International Steering Committee of ICSC

I wish all participants and accompanying persons very welcome to the 31st International Conference on Solution Chemistry (ICSC) and to Innsbruck and Austria. This conference series visits Austria for the fourth time, with the previous ones being the 4th ICNAS (International Conference on Non-Aqueous Solutions) in Vienna 1974 (chairman: Viktor Gutman), the 4th IS4I (International Symposium on Solute-Solvent-Solute Interactions) in Vienna 1978 (chairman: Viktor Gutman and B. Schuster), and 22nd the ICSC in Linz 1991 (chairman: Gerhard Gritzner). Solution chemistry has for a long time been a strong research area in Austria and it is therefore natural to return.

I am convinced that this conference, as the previous ones in this series, will report new interesting chemistry in a relaxed and friendly atmosphere. I encourage everyone to take some time off to chat with both old and new friends, and to learn more about the beautiful and historic city of Innsbruck and its surroundings. I encourage especially the younger scientists to take contact with older ones, do not be shy, we oldies will be more than happy to talk to you.

I give my sincere thanks to Professor Bernd Rode and his staff for all the preparation work for this conference. Without their efforts it would not have been possible to organize this kind of international meeting.

I wish you all a nice time in Innsbruck during 31st ICSC.

Ingmar Persson

Welcome Address by Prof. Dr. Dr. h.c. mult. Bernd Michael Rode Chairman of the Local Organising Committee of ICSC 2009

With great pleasure I and all members of the Local Organising Committee welcome so many participants from countries all over the world to our conference in Innsbruck. We hope that both the scientific and social contacts and events will make their stay with us a most rewarding and enjoyable one.

Looking at the list of participants we can witness with high satisfaction a very good mixture of well-established top scientists in the field, of excellent junior researchers and of ambitious and promising students, which should provide excellent conditions for a very fruitful dialogue among these groups and thus form a good starting point for further international co-operations and for setting new trends in solution chemistry.

The large number of contributions based on theoretical and computational approaches is certainly not just a consequence of the conference organisation by a theoretical group working for several decades in the field of solution chemistry, but signifies a continuous trend towards an increasing role of theoretical chemistry as an equivalent partner of experimental research, in particular with respect to liquid systems, and thus to a rapidly developing and rewarding co-operation between experimental and theoretical groups.

We are most grateful to all participants who are contributing to this conference, and we hope that they will return home with good memories and much inspiration for their future work.

Bernd Michael Rode

Programme on Friday, August 21st

09:30 - 10:00 Opening
Rode, Bernd M.
10:00 - 11:00 Inauguration Lecture PL-01
Wüthrich, Kurt

11:00 - 11:30 Coffee Break

11:30 - 11:50 Lecture OL-01
Yamaguchi, Toshio
11:50 - 12:10 Lecture OL-02
Majlesi, Kavosh
12:10 - 12:30 Lecture OL-03
Nuryono

12:30 - 14:30 Lunchtime

14:30 - 15:30 Highlighted Lecture PL-02
Kitagawa, Susumu
15:30 - 16:00 Invited Lecture SL-01
Steinhauser, Othmar
16:00 - 16:20 Lecture OL-04
Shalaev, Evgenyi

16:20 - 16:50 Coffee Break

16:50 - 17:10 Lecture OL-05
Bohinc, Klemen
17:10 - 17:30 Lecture OL-06
Waghorne, Earle
17:30 - 17:50 Lecture OL-07
Magalhães, Maria Clara

18:30 Reception

Programme on Saturday, August 22nd

09:00 - 10:00 Highlighted Lecture PL-03
Xantheas, Sotiris
10:00 - 10:30 Invited Lecture SL-02
Sanchez Marcos, Enrique

10:30 - 11:00 Coffee Break

11:00 - 11:30 Invited Lecture SL-03
Hofer, Thomas
11:30 - 11:50 Lecture OL-08
Túri, László
11:50 - 12:10 Lecture OL-09
Nezbeda, Ivo
12:10 - 12:30 Lecture OL-10
Holovko, Myroslav

12:30 - 14:30 Lunchtime

14:30 - 15:00 Invited Lecture SL-04
Vlachy, Vojko
15:00 - 15:20 Lecture OL-11
Dufreche, Jean-Francois
15:20 - 15:40 Lecture OL-12
Pranowo, Harno
15:40 - 16:00 Lecture OL-13
Hantal, Gyorgy
16:00 - 16:20 Lecture OL-14
Hannongbua, Supot

16:20 - 16:50 Coffee Break

16:50 - 18:30 Poster Session I
Posters 100 - 199
16:50 - 17:50 ICSC Meeting
Room IGLS

19:30 Concert

Programme on Sunday, August 23rd

09:00 - 09:30 Invited Lecture SL-05
Laubereau, Alfred
09:30 - 10:00 Invited Lecture SL-06
Bakker, Huib
10:00 - 10:30 Invited Lecture SL-07
Fábián, István

10:30 - 11:00 Coffee Break

11:00 - 11:20 Lecture OL-15
Wakisaka, Akihiro
11:20 - 11:40 Lecture OL-16
Umebayashi, Yasuhiro
11:40 - 12:00 Lecture OL-17
Kimura, Takayoshi
12:00 - 12:20 Lecture OL-18
Atik, Zadjia

12:30 - 14:00 Lunchtime

14:30 Excursions
Excursion A: Hafelekar Mountain, Victor Franz Hess Laboratory
Excursion B: Silver Mine Schwaz, Swarovski Crystal Worlds Wattens

Programme on Monday, August 24th

09:00 - 10:00 Highlighted Lecture PL-04
Persson, Ingmar
10:00 - 10:30 Invited Lecture SL-08
Soper, Alan

10:30 - 11:00 Coffee Break

11:00 - 11:30 Invited Lecture SL-09
Marcus, Yitzhak
11:30 - 11:50 Lecture OL-19
Malikova, Natalie
11:50 - 12:10 Lecture OL-20
Waluyo, Iradwikanari
12:10 - 12:30 Lecture OL-21
Torapava, Natallia

12:30 - 14:30 Lunchtime

14:30 - 15:00 Invited Lecture SL-10
Smiechowski, Maciej
15:00 - 15:20 Lecture OL-22
Chandra, Amalendu
15:20 - 15:40 Lecture OL-23
David, S.Theodore
15:40 - 16:00 Lecture OL-24
Puhovski, Yurii
16:00 - 16:20 Lecture OL-25
OPCW Representative

16:20 - 16:50 Coffee Break

16:50 - 18:30 Poster Session II
Posters 200 - 299

18:30 Banquet

Programme on Tuesday, August 25th

09:00 - 09:30 Invited Lecture SL-11
Hefter, Glenn
09:30 - 10:00 Invited Lecture SL-12
Ishiguro, Shin-ichi
10:00 - 10:20 Lecture OL-26
Billard, Isabelle
10:20 - 10:40 Lecture OL-27
Lyashchenko, Andrey

10:40 - 11:10 Coffee Break

11:10 - 11:30 Lecture OL-28
Schröer, Wolffram
11:30 - 11:50 Lecture OL-29
Turq, Pierre
11:50 - 12:10 Lecture OL-30
Fujii, Kenta
12:10 - 12:30 Lecture OL-31
Buchner, Richard

12:30 - 14:30 Lunchtime

14:30 - 15:00 Invited Lecture SL-13
Bernkop-Schnürch, Andreas
15:00 - 15:20 Lecture OL-32
Wachter, Wolfgang
15:20 - 15:40 Lecture OL-33
Kanzaki, Ryo
15:40 - 16:00 Lecture OL-34
ICSC-32 (2011) - Turq, Pierre
16:00 - 16:20 Closing
Rode, Bernd M.

Highlighted Lectures

Solution NMR structures of Proteins - from Structural Biology to Structural Genomics

Wüthrich, Kurt

The Scripps Research Institute, La Jolla, CA, USA;
and ETH Zürich, Zürich Switzerland
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Solution NMR spectroscopy can provide atomic resolution three-dimensional protein structures under conditions close to the physiological milieu in body fluids. Here we discuss the role of this technique in the newly emerging area of structural genomics.

In today's post-genomic era, with the availability of the complete DNA sequences of a wide range of organisms, structural biologists are faced with new opportunities and challenges in "structural genomics". In contrast to classical structural biology, research in structural genomics is focused on gene products with unknown structures, unknown functions, and minimal similarity to previously studied proteins. A precisely formulated goal of structural genomics is to determine representative three-dimensional structures for all protein families, which requires 'high-throughput' technology of protein production and structure determination. The long-term outlook is to predict physiological protein functions from knowledge of three-dimensional structures. The California-based Joint Center for Structural Genomics (JCSG; PI Dr. Ian A. Wilson) is one of the four large-scale consortia in the NIH-funded Protein Structure Initiative (PSI). The JCSG developed and operates an extensively automated high-throughput pipeline for protein production, crystallization and crystal structure determination. However, there remain gaps in the coverage of protein fold space that are due to certain proteins not being readily amenable to crystal structure determination. My research team (the "NMR-Core") works on filling such gaps with a 'high-throughput' approach, which involves novel strategies of target selection as well as new technology for NMR structure determination. In addition to *de novo* protein structure determination, NMR in solution can generate data on protein stability and dynamics, and on intermolecular interactions. NMR thus has an exciting role also in longer-term challenge that should lead from the expanding protein structure universe to new insights into protein functions and other aspects of chemical biology.

The JCSG is supported by the National Institute of General Medical Sciences, Protein Structure Initiative: Grant U54 GM074898.

CHEMISTRY OF POROUS COORDINATION POLYMERS

Kitagawa, Susumu

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The recent advent of porous coordination polymers (PCPs) or metal organic frameworks (MOFs), as new functional microporous adsorbents and reaction nanovessesl, have attracted the attention of chemists due to scientific interest in the creation of unprecedented regular nano-sized spaces and in the finding of novel phenomena, as well as commercial interest in their application for storage, for separation and in heterogeneous catalysis.[1] The key to the success of CP synthesis with the aid of self-assembly process in solution is the design of molecular building blocks that direct the formation of the desired architectural, chemical, and physical properties of the resulting solid-state materials. The development of the chemistry is summarized as the folowing targets along the time course; (1)robust frameworks[2], (2)high surface area and porosity,[3,4] (3)functionalization of pores,[5] (4)flexible frameworks.[6]

In the pores of PCPs, the walls, composed of atoms, molecules and portioned spaces, have very strong effects on the orientation, correlation and assembled structure of guest molecules. Researchers can therefore control the state of the guest molecules by changing the size, shape and material of the walls. We have developed PCPs by exploiting the advantages of CPs: (1)structural designability, (2)regularity and (3)flexibility. To date PCPs are found in fledgling, Phase 1 developments, in which pore functions are explored individually. The next challenge is to create novel porous materials in which several of the above-mentioned pore functions are integrated into the same material and in which the pore function can be changed in response to the surrounding environment. For this purpose we need to develop the science, and in particular the chemistry, to better understand the relationship between the structure and function of porous materials, and thus open up the era of Phase II in PCP research.

1.Kitagawa, S. et.al., Angew. Chem. Int. Ed,, 2004, 43, 2334.
2. Kondo, M. et.al, Angew.Chem.Int.Ed. 1997, 36,1725.
3. Chae,H.K.. et.al., Nature, 2004, 427, 523.
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6. Kitagawa,S. and Kondo, M. Bull. Chem. Soc. Jpn.1998, 71, 1739.

An ab-initio based transferable interaction potential for water: Simulations of water clusters, liquid water, ice & hydrate networks

Xantheas, Sotiris

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We present recent progress in the development of the flexible, polarizable interaction potential for water (TTM3-F) [1-5] with emphasis in describing the macroscopic structural, thermodynamic, spectral and transport properties of aqueous condensed environments. The interaction potential is parametrized from the results of high-level electronic structure calculations of water clusters and it is based on smeared Coulombic, dipole-dipole and van der Waals interactions. It represents an attempt to approximate the Born-Oppenheimer PES and it is therefore suitable for quantum rather than classical statistical mechanical simulations. We will present results with the new potential for the structures and binding energies of water clusters as well as converged nuclear quantum statistical simulations for the second virial coefficient, the diffusion coefficient for H_2O and D_2O, the density anomaly, the dielectric constant, the enthalpy and the infrared (IR) and 2-D IR spectra of liquid water.

In the last part of the talk I will discuss recent advances in the construction of low-energy networks for the structure I (sI) hydrate lattice from a bottom-up approach [6] based on the low energy networks of the constituent dodecahedron $(H_2O)_{20}$ (D-cage) and tetrakaidecahedron $(H_2O)_{24}$ (T-cage) [7]. The D- and T-cages are the building blocks of the (sI) hydrate host lattice and our results can furthermore be used to obtain the low-energy hydrogen bonding networks of those periodic structures allowing for a realistic modeling of the accommodation of guest molecules in clathrate hydrates.

References:

1. C. J. Burnham and S. S. Xantheas, *J. Chem. Phys.* **116**, 1479 (2002).
2. C. J. Burnham and S. S. Xantheas, *J. Chem. Phys.* **116**, 1500 (2002).
3. C. J. Burnham and S. S. Xantheas, *J. Chem. Phys.* **116**, 5115 (2002).
4. G. S. Fanourgakis and S. S. Xantheas, *J. Phys. Chem. A* **110**, 4100 (2006).
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7. S. Yoo, M. V. Kirov and S. S. Xantheas, J. *Amer. Chem. Soc.* **131**, 7564 (2009).

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Hydrated Metal Ions in Aqueous Solution How Regular are Their Structures

Persson, Ingmar

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The structure of the hydrated metal ions in aqueous solution plays important roles for their physical-chemical properties as reactivity and reaction kinetics. The structures of the most hydrated metal ions are now established in aqueous solution. In most cases the aqua complexes are highly symmetric having tetrahedral, octahedral, square antiprismatic and tricapped trigonal prismatic configuration. However, some metal ions display lower symmetries due to distortions of electronic or steric character. An overview of the hydrated metal ions in aqueous solution will be given with special emphasis on the metal ions with lower symmetry. Hydrated metal ions may have lower symmetry due to i/ Jahn-Teller or second order Jahn-Teller distortion, ii/ water-deficit due to steric restrictions and extensive hydrogen bonding, iii/ stereo-active lone electron pairs and iv/ positively charged oxo metal ions.

Invited Lectures

Relaxation of hydration shells in aqueous solutions of oligosaccharides, peptides and proteins.

Steinhauser, Othmar

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The behaviour of water in these complex systems is of great diversity depending on the degree of vicinity to the respective solute. Therefore it is decomposed into first and second hydration shells as well as bulk water.
Instead of the traditional way defining hydration shells via pair correlation functions and somewhat arbitrary distance thresholds the method of Delauny tesselation is used for a parameter-free decomposition of the space around the solute.
Hydration shells and bulk water are analyzed at both levels, the molecular and the mesoscopic. In the latter case dielectric relaxation places a central role and the importance of cross terms becomes obvious.
In order to cope with the complex time behaviour multi-exponential as well as Kohlrausch-William-Watts functions are used to characterize the time correlation functions.
Upon Fourier transformation of the latter the spatial Voronoi decomposition finally results in a decompostion of dielectric spectra which is intensively applied to interpret experimental spectra.

Solving the Hydration Structure of Metal Ions in Solution by Coupling MD simulations and X-ray Absorption Spectroscopies

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A primary point in the understanding of the physicochemical properties of electrolyte solutions of transition metal ions is the determination of their solvation structure. Among the reduced number of experimental techniques which can supply information on the environment, X-ray Absorption Spectroscopy (XAS) has gained importance during the last decades. Main advantages of this technique are which can supply information on the ion environment, it is element-specific, (local structure around the ion can be solved), and it can be applied to systems with a low concentration in the metal ion. However, the XAS data analysis is not free of difficulties as the high correlation among factors affecting the amplitude and the large number of multiple scattering paths which may contribute to the global signal. During the last fifteen years implementations of models for the absorption phenomena based on the inclusion of independent information derived from quantum mechanics and computer simulations for both EXAFS and XANES spectra have been incorporated to help in the XAS data analysis. The theoretical description of highly-charged metal cations in solution is a challenge topic due to the concurrence in its modelling of a set of factors which may strongly affects to their physico-chemical description, such as quantum-mechanical description, modelization of the condensed medium effects, particularly, the metal-ion solvent interactions, competition of hydrolysis and polymerization processes, dynamical factors, etc. This contribution presents a set of cases studied by classical and ab initio Molecular Dynamics techniques, where aqueous solutions of the trivalent Cf(III) and square-planar Pt(II) and Pd(II) complexes are modelized.[1] The structural information theoretically obtained from the previous computations is employed together with ab initio multiple-scattering codes of XAS (FEFF) to simulate their EXAFS and XANES spectra in solution.[2] The synergy derived from this theoretical-experimental combination is explored and discussed.

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Characterisation of non-spherically solvated ions via molecular simulations

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The majority of monoatomic ions exhibit a spherically symmetric potential resulting in solvation structures reflecting this high degree of symmetry. However, some systems are known to have potentials with lower symmetry leading to the formation of anisotropic hydration structures. Prominent examples are the hydrated Cu(II), Pd(II) and Pt(II) ions. The interaction of these ions with the solvent does not show a spherical symmetric pattern. Due to the existence of a preferential directions, the application of spherical symmetric potentials in simulation studies cannot reflect this behavior in a proper way, whereas a quantum mechanical treatment is capable to account for such anisotropic effects.

In addition to the obstacles encountered for the treatment of the intermolecular interactions, an appropriate analysis of the spatial arrangement of ligands surrounding these ions is of special interested. Commonly pair- and threebody correlation functions are utilised to visualise structural properties. As simulation studies give access to the coordinates of all atoms as a function of time, it is possible to utilise advanced analysis schemes taking into account the preferential directions of the solvate structure. Radial-angular distributions functions are versatile tools to illustrate anisotropic solvation by utilising an individual analysis of distinct regions in the vicinity of the ion.

This class of analysis tools are of special interest interesting for composite species due to the existence of an preferential direction on the one hand and the existence of various overlapping pair correlation functions. The mercury(I) dimer and the cyanide ion will serve as examples demonstrating that pair potentials could lead to an improper representation of the structural properties while segmented radial distribution functions enable the full characterisation of the system of interest.

Ionenes, hydrophobic polyelectrolytes with unusual solution thermodynamic properties

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Aliphatic ionenes are alkyl polymer chains in which different numbers x,y of methylene groups separate quaternary ammonium groups. They are ideal molecules for studying the balance between hydrophobic and charge effects in water. The experimental results are available for 3,3, 4,5, 6,6, and 6,9 ionenes in aqueous solutions with halide ions (see [1,2] and the references therein). The conclusions are: i) the osmotic and activity coefficients are considerably lower than predicted by the implicitwater cellmodel; the disagreement increases with the increasing hydrophobicity. ii) Chlorine counterions bind more strongly to the ionenes as bromines. iii) Enthalpies of dilution of 3,3 and 4,5 ionene solutions with bromide and chloride counterions (chaotropes) are endothermic, while the corresponding solutions of more hydrophobic 6,6 and 6,9 ionenes produce exothermic effect. The heat of dilution measurements for 3,3 and 6,6 ionene fluoride (kosmotrope) are exothermic. iv) The implicitwater models, such as cell model or Mannings approach, predict for this effect to be exothermic for all the ionenecounterion combinations.

We present a molecular dynamics simulation, in explicit SPC/E water, of a solution of aliphatic 3,3 [3] and 6,6 ionene oligocations with sodium coions, and fluorine, chlorine, bromine, or iodine counterions. The 6,6 ionene, which has more hydrophobic groups than the 3,3 ionene, shows more drying; i.e., the waters are displaced more from the polymer surface. Also, we find that the large ions, such as iodine, act like hydrophobic groups insofar as they bind to ionene's methylene groups, though the effect is weak. Smaller ions, like fluorine, bind water tightly. The water mediated attraction between fluorine ions is enhanced in presence of weakly charged 6,6 ionene molecules. This effect may additionally reduce the osmotic pressure in such systems. The results can explain some experimental trends [1,2,4] in ionene solutions and weakly charged polyelectrolytes in general [1].

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Electron detachment from anions in aqueous solutions studied by two and three pulse femtosecond spectroscopy

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The photoinduced charge transfer in hydrogen-bonded systems is of major importance in life sciences. Of special interest are the halogenide and the hydroxide anions in water. We report novel data on the electron photodetachment derived from pump-repump-probe spectroscopy on the 100-fs to 1-ns time scale. The anions are excited by 1-photon absorption at 202 nm and the subsequent relaxation, governed by equilibration, recombination and dissociation, is studied in a broad spectral probing range extending from 450 nm to 2500 nm. The electrons are released from the initially populated CTTS state via at least two intermediates assigned to solvent-separated neutral-electron pairs followed by recombination and dissociation processes to the final hydrated electrons. An additional repump pulse at 810 nm is used for secondary excitation of the intermediate species and shown to manipulate the recombination channel thus increasing the final yield of long-lived solvated electrons. With this technique the solvent-separated pairs can be spectroscopically distinguished from fully detached electrons and the effective lifetime of the pairs be determined. For Br^- a pair lifetime of 19 ± 1 ps is found at 298 K. The measured temperature dependence of the time constant suggests a free energy barrier for pair dissociation of ΔG = 0.15 ± 0.02 eV. Similar results were obtained for other halogen anions.
For OH^- in H_2O and OD^- in D_2O notably faster kinetics are observed with two time constants for pair recombination. Values of 0.7 ± 0.2 ps and 15 ± 1 ps (1.0 ± 0.2 ps and 18 ± 1 ps, respectively for OD^-) are measured at room temperature. The fast recombination channel for the $OH:e^-$ (and $OD:e^-$) pairs in water does not exist for the halogen cases and is reported for the first time. The mechanism will be discussed and compared with results for the photoionization of neat water.

Femtosecond study of the reorientation of water in solutions of ions and hydrophobes

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We study the dynamics of water molecules in solutions with polarization-resolved femtosecond mid-infrared spectroscopy (fs-IR) and terahertz (THz) time-domain spectroscopy (THz-TDS). In the fs-IR experiments, we measure the orientation dynamics of the OD group of HDO molecules dissolved in H_2O, by probing the anisotropy dynamics of the excitation of the OD stretch vibration. In the THz-TDS studies, we determine the orientation dynamics of the permanent dipole moment of the water molecule, i.e. the bisector of the water molecule, by probing the polarization response of the solution to a far-infrared electric field. The combined application of the two techniques to the same solution provides detailed information on the molecular reorientation of solvating water, because the two techniques probe the reorientation of different axes of the water molecule.

In the THz experiments, we observe that cations like Mg^{2+} lead to a strong slowing down of the reorientation of a number of water molecules, while the effect of anions is much smaller. Interestingly, in the fs mid-IR experiments it is the other way round: cations have little effect, whereas anions like ClO_4^- and SO_4^{2-} slow down the reorientation of the water molecules in their hydration shells. These results show that water molecules in the hydration shells of ions are hindered in their reorientation, but only in certain directions. For instance, for a water molecule hydrating a cation, the permanent dipole moment is immobilized as this vector is pointing away radial from the cation, leading to a depolarization effect in THz-TDS. However, rotation of the OD/OH around the permanent dipole moment is then still possible, leading to a bulk-like rotation time of 2.5 ps observed with fs-IR. We also observe an interesting cooperative effect of cations and anions on the reorientation of water. For solutions of a weakly interacting anion like ClO_4^-, the effect on the reorientation of water does not at all depend on the nature of the cation. However, for a more strongly interacting anion like SO_4^{2-}, the fraction of slow water increases with increasing interaction strength of the cation with water. This observation may lead to a new view of the Hoffmeister effect of ions on the structural dynamics of water.

For hydrophobic molecular groups we observe a strong effect with both fs-IR and THz-TDS, showing that for water molecules in the hydrophobic hydration shell the orientation mobility of the permanent dipole and the OD/OH groups are both strongly slowed down.

Light Induced Multistep Redox Reactions: The Diode Array Spectrophotometer as a Photoreactor

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Diode array spectrophotometers are commonly used in experimental chemistry. Their advantage over traditional scanning instruments is that they can record high-quality spectra in a relatively short time. However, an intense polychromatic light beam illuminates the sample in such instruments, which may initiate photochemical reactions. Our recent work has shown that this effect can be used for studying photoinitiated processes in order to obtain mechanistic information on complex reactive systems. (1-5) This will be illustrated in the presentation by kinetic studies on various autoxidation reactions of sulfur(IV) and the autocatalytic oxidation of iodine by chlorate ion.

The cerium(III) and the iodide ion catalyzed, photoinitiated oxidation of sulfur(IV) by oxygen has been studied in acidic aqueous solution. The direct reaction is a slow process, while a chain mechanism proved to be operative in the catalytic reactions. The role of light is only to initiate the chains and 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. Cerium(III) acts as both a photoactive absorbing species and a catalyst for the propagation steps. In the iodide ion system, hydrated sulfur dioxide is also a photoactive absorbing species. Radical chain mechanisms interpret the experimental observations in both cases. The most important chain carriers are sulfite, sulfate, and peroxomonosulfate ion radicals.

Exotic phenomena in the iodine-chlorate ion system have been reported recently. (5, 6) The reaction does not occur under thermal conditions in the dark. The reaction is triggered by illumination with light which produces I• atoms. The overall reaction is catalyzed by HOCl as well as ClO2– formed as reactive intermediates, and a kinetic model will be presented to interpret all experimental findings.

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Water the solvent: latest insights into its structure from diffraction experiments.

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Water occupies an inordinate amount of space in the scientific literature due to its ubiquity in our environment and importance in many different fields of science. As part of this onslaught of information the structure of water has been investigated extensively by many different techniques leading to a plethora of results so that even today it is impossible to ascertain which, if any, can be trusted. Perhaps two of the more bizarre recent results are that the structure of water is affected by relatively modest magnetic fields, (J. Appl. Phys., vol. 88, p. 1802 (2000)), and that the structure of water is altered by sunlight (Japan. J. of Appl. Phys., vol. 46, p. 333 (2007)). This change in the structure of water due to sunlight appears unlikely: in Britain for example the rain during the day is just as wet as the rain at night!

In principle diffraction experiments, particularly neutron diffraction experiments, probe the structure of bulk water at the level of the molecular correlation functions. This is because the neutron is both highly penetrating, so sees the liquid well away from any surfaces, and because the neutron is scattered by the atomic nucleus, and so is largely unaware of the associated electronic structure. Hence the neutron experiment in principle probes directly the theoretically interesting site-site correlation functions. Indeed there is probably no other experimental probe of structure which has such a simple and direct relationship with theoretical quantities. Unfortunately this apparent simplicity is marred by the fact that in the diffraction pattern all the relevant site-site terms get added together by weighting functions which depend on the proportion and scattering properties of the nuclei in question, and the fact that hydrogen in particular recoils under neutron impact, which distorts the scattering pattern in a way that is hard to estimate reliably.

Recently we have added x-ray diffraction to our armoury of techniques for disentangling the site-site terms from diffraction data. X-rays, which are scattered by the electrons not the nuclei, come with their own set of problems, the most serious of which is that we don't know a priori how the electrons in the liquid are distributed with respect to the nuclei. The talk will review some of the latest results using these probes and will attempt to identify the amplitude of uncertainties in the extracted site-site radial distribution functions for water.

The effect of ions on the structure of water: structure-making and breaking

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It is generally accepted that water differs from other liquids at ambient conditions by having an extensive three-dimensional network of hydrogen bonds. There is no agreement, however, on the quantitative aspect of this phenomenon, that is, on the average number of hydrogen bonds per water molecule it is engaged in. Nor, indeed, is there agreement on how an intact hydrogen bond is to be distinguished from a broken or non-existing one. Some reasonable suggestions for the definition of a hydrogen bond in liquid water, hence of the average number of such bonds per water molecule (the structure of water) are presented.

When an electrolyte is dissolved at high dilution in water, the ions are expected to change the water structure in their vicinity, due to their space occupation, their large electric field, ion-dipole interactions, and possible hydrogen bonding with water molecules. The orientation of the water molecules in the first hydration shell of an ion certainly differs from that in bulk water, but there arises the question to what extent such structural changes prevail beyond this hydration shell.

A large body of evidence, both static (thermodynamic) and dynamic, experimental and computational, exists that ions at high dilution in water do affect the water structure beyond that of the molecules immediately adjacent to them. The experimental evidence comes from the entropies of hydration of ions and their transfer Gibbs energies from light to heavy water, from the activation energy of water molecule diffusion, viscosity, and NMR and dielectric relaxation, among other methods. Computation by means of combined quantum mechanics and molecular dynamics leads to similar results. Moreover, there is agreement among the different methods concerning the effects of the ions on the water structure.

The conclusion is that certain ions diminish the extent of hydrogen bonding in their dilute solutions in water, and such ions are called structure-breakers, whereas other ions enhance the extent of hydrogen bonding, thus being structure-makers. Quantitative measures of the magnitude of these effects are presented, allowing the arrangement of the ions in a hierarchy of their water structural effects. This hierarchy is analogous to a certain degree to the well-known Hoffmeister series, but the latter pertains to a non-isotropic situation, contrary to the effects of ions on the structure of water in dilute solutions.

Vibrational spectroscopy of HDO as a probe of solute hydration - a survey of recent investigations

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Water is certainly the most important of solvents and the studies of hydration mechanisms have direct consequences for our understanding of fundamental biochemical processes. The investigation of biomolecules in water poses many difficulties, however, due to the appearance of many cooperative or competitive effects, which are almost impossible to resolve individually. Therefore, it is desirable to study simpler model compounds, which present an isolated type of water-solute interaction connected with the presence of a specific functional group.

Vibrational spectroscopy is an ideally suited tool for the study of solute hydration. Nevertheless, water is commonly considered by spectroscopists a difficult solvent to work with. However, when tiny amount of D_2O is introduced into H_2O or vice versa, HDO is formed almost quantitatively. By using this isotopic dilution technique certain problems connected with measurement of infrared spectra of water may be circumvented. Particularly, the isotopic decoupling of stretching vibrational modes simplifies interpretation of the spectra.

Recently, time-dependent femtosecond infrared spectroscopy is booming, offering details on vibrational dynamics of aqueous systems. The classic static measurements can still, however, provide lots of valuable data. Following some early investigations, systematic studies from the 1980s and early 1990s gave a vast amount of data, concerning mainly ionic hydration. These measurements were performed primarily in the research group of Professor Lindgren at Uppsala University and simultaneously in our laboratory. The analysis method based on the quantitative version of differential spectra technique, developed independently in these two groups, allows separation of the spectrum of solute-affected HDO from the bulk solvent on the basis of spectra of entire solution series.

Preliminary results obtained for aqueous non-electrolytes encouraged us to pursue this task further. At the same time, new ionic systems became available for study and interpretation with our thoroughly tested method of data analysis. Therefore, the two simultaneous paths that are currently followed in our group are on the one hand simple model systems for biomolecules and on the other hand more problematic ionic solutes, such as the hydrated proton or the hydroxide anion. The amount of spectral data hitherto collected by us is sufficient to draw general conclusions concerning both electrolytes and non-electrolytes in aqueous solutions.

Chemical Speciation and Other Difficulties in Ionic Liquids

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Understanding the nature of room temperature ionic liquids (RTILs) presents many difficulties to experimentalists and molecular modellers alike. Undoubtedly RTILs are not just simple mixtures of free cations and anions, as is indicated for example by their relatively low electrical conductivities and high viscosities, but their real character remains obscure. Dielectric relaxation spectroscopy (DRS), a form of MW spectroscopy in and around the GHz region, is a very powerful tool for investigating the properties of RTILs. DRS not only provides the only means of directly measuring the dielectric constant of conducting fluids like RTILs but also yields information on the nature and dynamics of any dipolar species present. In addition to its sensitivity to ion pairs DRS is useful for detecting mesoscale or cooperative interactions that are likely to be important for RTILs but which are difficult to observe with most other techniques. Detailed DRS investigations have been made of a range of imidazolium salts to unravel the spectral contributions associated with particular molecular-level species. Measurements have also been made on neat RTILs as a function of temperature and on mixtures of RTILs with representative molecular solvents. Contrary to popular belief there is no evidence in the neat ILs for the existence of discrete ion pairs; such species appear to exist only at high dilution (typically $x_{IL} < 0.1$) in molecular solvents. Larger aggregates form at higher IL concentrations in molecular solvents and probably in the neat RTILs although the exact nature of these species is unclear at present. At high xIL there is evidence from DRS of microheterogeneous phase separation in some systems but the aggregates formed do not appear to be micelles, at least for ILs with short alkyl chain substituents. The DR parameters for IL/co-solvent mixtures studied to date show no evidence for a sharp transition between electrolyte-solution-like and molten-salt-like behaviour as has been claimed by some.

Structure, Solvation and Acid-Base Property in Ionic Liquids

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Ionic liquids (ILs), which are mainly composed of bulky organic cations and inorganic anions, are attracted attention as novel solvents in various fields of chemistry, as well as applications. We know that reactions, such as acid-base, complexation and redox reactions, in solution strongly depend on the solvent. In molecular solvents, ions are solvated, and solvent molecules desolvate an ion upon reaction, and the solvent molecules are then accommodated in the bulk structure. Solvation and liquid structure are thus essential to understand the solvent effect on reactions in solution. The same may also applies to ions and moleules in ILs. Liquid structure, solvation and reaction in ILs may be essentially different from those in molecular liquids, as solvent ions of ILs are bulky and flexible to easily change their conformation. Solvent cations consist of polar and nonpolar sites, like surfactant molecules, which may yield heterogeneous solvent structure at nano-scale level. Solvent anions, the conjugate base of super acids, cannot coordinate to the metal ion in molecular solvents, whereas they can in ILs. However, we dont know well the nature of ILs as the solvent in view of solution chemistry.

Therefore, to understand reactions in ILs, we studied molecular conformation and liquid structure of some protic and aprotic ILs, as well as acid-base properties and solvation of metal ions. In the present talk, we demonstrate our experimental and theoretical approaches to the conformational equilibrium of some cations and anions of ILs, and their liquid structures. The bis-trifluoromethanesulfonyl) amide anion hardly coordinate to the metal ion in molecular liquid, but it binds to the metal ion in ILs, and the solvation number and conformation will be shown. Acid-base property of solvent is essential to reveal pH scale of protic ILs. We also demonstrate the pH scale of some protic ILs, and the acidity and basicity of some acid and base in the solution.

Oral Drug Delivery: How do chemical reactions in the gastrointestinal tract influence the therapeutic potential of drugs?

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The oral administration is by far the most favored one. The majority (84%) of 50 most-sold pharmaceutical products in US and Europe markets are given orally. Numerous drugs, however, cannot be administered orally because of inactivation in gastrointestinal (GI) fluids. This inactivation is based on various chemical reactions including hydrolytic cleavage, enzymatic degradation and thiol/disulfide exchange reactions.

A hydrolytic cleavage is taking place in particular at low pH. Various antibiotics, for instance, are hydrolysed in the stomach. Strategies to overcome this problem are primarily based on enteric coated drug delivery systems.

Various classes of drugs such as therapeutic peptides and nucleic acids are enzymatically degraded by proteases/peptidases and nucleases, respectively. Proteases/peptidases are on the one hand based on luminally secreted proteases including pepsin, trypsin, chymotrypsin, elastase and caboxypeptidase A and B and on the other hand on membrane bound peptidases including various endo- as well as amino- and carboxypeptidases. In the colon numerous additionally enzymes originating from the local microflora have to be taken into consideration. In terms of nucleases the enzymatic barrier is much less characterized.

Furthermore ester bonds are cleaved by esterases such as lipases and proteases/peptidases exhibiting also esterase activity. Strategies to overcome a presystemic enzymatic degradation include the use of low molecular mass and polymeric enzyme inhibitors as well as various formulation approaches such as liposomal formulations, micro- and nanoparticles as well as matrix tablets protecting the incorporated drug towards an enzymatic attack.

In case of thiol/disulfide bond bearing drugs thiol/disulfide exchange reactions in particular with glutathione can inactivate them in the GI-tract.

Food intake can strongly alter the enzymatic activity in the GI-tract and can lead to further chemical reactions between drugs and certain food components.

A detailed knowledge on such chemical reactions taking place in the GI-tract and promising strategies to avoid such reactions contribute to the development of more efficient and save oral therapeutic systems.

Oral Contributions

Structure and Dynamics of Low Temperature Confined Water

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Structure and dynamic properties of water confined in nanometer space have recently drawn much attention because confined water can help us to understand the function of interfacial water that plays a vital role in biological membranes. In particular, water confined in pores (the diameter less than ~20 Å) is stable down to 140 K, not attainable in bulk water, and such low temperature confined water would provide us a hint for understanding the dynamical transition of protein hydration related to onset of activation of proteins. In the present study, water was adsorbed in monolayered and capillary-condensed state in MCM-41 with a pore diameter 21 Å that has highly controlled cylindrical channels and hydrophilic surface of Si-OH groups. Thermal and phase behaviors of confined water were examined by DSC, heat capacity, and FTIR measurements. These data indicated some phase transition at ~230 K. Direct structure determination of supercooled confined water was made by in-situ X-ray diffraction and neutron diffraction with isotopic substitution methods. X-ray radial distribution functions have shown that the structure of capillary condensed water in a temperature range 273~230 K is very similar to that of high-density amorphous ice in bulk, whereas that at 220~190 K is analogous to that of low-density amorphous ice in bulk. The corresponding dynamic properties of supercooled confined water were investigated by quasi-elastic neutron scattering and neutron spin echo measurements. The neutron spin echo data on both monolayered and capillary-condensed water have shown a dynamical crossover in the relaxation time at ~230 K from the Vogel-Fulcher-Tamman type (fragile liquid) behavior above 240 K to the Arrhenius type (strong liquid) one below 220 K. Based on all the information obtained, the structure, dynamic properties, and function of supercooled confined water will be discussed in connection with the interfacial water in a biological system.

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Application of Kamlet-Taft Equation for Determination of Solvatochromic Parameters in Mo(VI) + EDDA Complex

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It is proposed that the solvent effect depends directly on the solvent polarity. On the other hand, solvent dipole moments are not sufficient for measuring the solvent polarity therefore it is stated that the polarity of a solvent is determined by its solvation capability for reactants and activated complexes as well as for molecules in their ground and excited states. Thus solvation power depends on all specific and nonspecific intermolecular forces between solvent and solute molecules. Various empirical solvent polarity parameters have often been used fairly effectively to describe the influence of solvents on physicochemical solute properties of different kinds. One particularly useful set consists of completely lewis acid/base solvent parameters. Until now the complexity of solute-solvent interactions prevented the derivation of generally applicable mathematical equations that make it feasible to calculate the equilibrium constants of reactions carried out in solvents at different polarity, but one of the well-known equations which works well in this field is Kamlet-Taft equation. It was found for example, by analysis of the variation of Kamlet-Taft β values for mixtures of methanol and other organic solvents that an important factor influencing the basicity of solvent mixtures is due to order/disorder processes; particulary in binary mixtures of protic with non-hydrogen bond donor solvents. Therefore by pursuing our systematic study on some transition metal aminopolycarboxylic acid complexes at different ionic strengths[1-4], the stability constants of the 1:1 complex formed between Mo(VI) and EDDA were calculated at 25 °C and constant ionic strength 0.1 mol dm^{-3} sodium perchlorate in different compositions of methanol + water by a combination of potentiometric and UV spectrophotometric methods. The influence of the solvent on the stability of the complex was discussed on the basis of the correlation results and the contribution of α, β and π^* parameters. It was found that the parameters contributions are in the following order: $\beta > \pi^* > \alpha$.

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Adsorption of calcium(II), lead(II) and silver(I) on sulfonato-silica hybrid prepared from rice hull ash

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In this research, adsorption of Ca(II), Pb(II) and Ag(I) in aqueous solution onto sulfonato-silica hybrid (SSH) prepared from rice hull ash (RHA) has been studied. The preparation of SSH adsorbent was carried out by oxidation of mercapto-silica hybrid (MSH) with hydrogen peroxide (H_2O_2) solution 33 %. MSH was prepared, via sol-gel process, by adding 3 M hydrochloric acid solution to mixture of sodium silicate (Na_2SiO_3) solution and 3(trimethoxixilyl)1propanthiol (MPTS) to reach pH of 7.0. Solution of Na_2SiO_3 was generated from destruction of RHA with sodium hydoxide solution followed with heating at 500 ^oC for 30 min. The SSH produced was characterized with Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analyser, energy dispersive X-ray (EDX) spectroscopy and determination of ion-exchange capacity for sodium ion (Na^+). The adsorption of Ag(I) and Ca(II) were conducted in a batch system in various concentrations for one hour. The adsorbent ion was calculated based on difference of concentrations before and after adsorption process determined using atomic absorbance spectrophotometric (AAS) method. The adsorption character was evaluated using model of isotherm Langmuir and Freundlich adsorption to calculate the capacity, constants and energy of adsorption. Result of characterization by EDX and FTIR showed qualitatively that SSH has been successfully synthesized which were indicated by appearance of characteristic absorbance of functional group namely silanol (SiOH), siloxane (SiOSi), methylene (CH_2) and disappearance of mercapto group (SH). The XRD data showed amorphous structure of SSH, similar to silica gel (SG) and SSH. The study of adsorption thermodynamics showed that oxidation of MSH into SSH increases the ion-exchange capacity for Na^+ from 0.123 to 0.575 mmol/g. The change functional group from silanol to mercapto and from mercapto to sulfonato increases the adsorption capacity of Ca(II). However, the capacity order of adsorbents for both ions of Pb(II) and Ag(I) in aqueous solution is MSH > SG > SSH. The adsorption energy of Ca(II) on the produced adsorbents SG, MSH and SSH indicates that interaction between adsorbent and investigated metal ions is dominated by physisorption, whereas the interaction for Pb(II) and Ag(I) involves chemisorptions.

Medium effects in chemical instability of amorphous pharmaceutical systems

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Many drug molecules are unstable in aqueous solutions. In such cases, a solid powder for reconstitution is usually chosen as a parenteral dosage form. Although such solids provide a better stability for drug molecules than solutions, chemical reactions may still occur at a measurable rate over the timeframe of weeks and months, especially if the drug is present in an amorphous state. As a result, significant R&D efforts are devoted to stability optimization, e.g., by choosing appropriate excipients and reducing residual water content to a low level.

Until recently, chemical reactivity in pharmaceutical glasses has been mainly considered from the molecular mobility perspectives, with molecular mobility expressed in various forms including the glass transition temperature, the rate of a "global" structural relaxation, and localized fast relaxation modes, to name a few. Indeed, relationships between molecular mobility and chemical instability are established for many amorphous solids of pharmaceutical interest. For example, development of a high-temperature annealing method, which is used to accelerate structural relaxation and slow down chemical reactivity in amorphous pharmaceuticals, represents one of the recent successes in practical applications of the "molecular mobility" concept.

It has been proposed, however, that, in addition to molecular mobility, other factors may contribute to chemical reactivity of amorphous solids. In this presentation, several examples are considered to investigate role of medium effects (as known in organic physical chemistry of solutions) in chemical reactions of pharmaceutical glasses. A model reaction, i.e., sucrose inversion, has been used to investigate several aspects of media effects as applied to amorphous systems, including role of acid-base relationships (expressed through the Hammett acidity function), and kinetic salt effects. In addition, hydrolysis of an experimental drug, Zoniporide, was studied to investigate role of water in chemical degradation of amorphous pharmaceuticals.

Interaction between charged surfaces induced by rod-like nanoparticles

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Highly charged systems could not be described by the mean field theory. More advanced methods have to be used in order to introduce the correlations between highly charged particles. In this work we focus on the system of highly charged surfaces (1), separated by a solution of nano-particles with spatially distributed charges (2). The nano-particles possess dipole or quadrupole moments. Our system is theoretically described by using functional density theory (3, 4). The minimization of the system is performed to obtain the equilibrium configuration of the system. The solution of the variational problem shows that orientational ordering of nano-particles in the field of the system give rise to attractive interaction between like charged surfaces (4). We showed that for sufficiently large dimensions of nanoparticles and large surface charge densities an attractive force between like surfaces arises due to the spatially distributed charges within the nano-particles. Recent measurements with multivalent rigid rod like particles will be discussed.

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Hydrogen Bonding to Nucleic Acid Bases

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Hydrogen bonding between the nucleic acid bases is central to the stability and functioning of both DNA and RNA with hydrogen bonding to the conjugate base and to water or protein molecules being significant.

The carbonyl region of the infrared spectra of the oxygen containing bases is extremely sensitive to changes in solvation, particularly hydrogen bond formation to the carbonyl oxygens, and so provides an effective tool for studying hydrogen bonding. Thus, we have investigated the stepwise formation of hydrogen (strictly deuterium) bonds to the oxygen atoms of bases to D_2O in DMSO solution where the N-H protons are strongly solvated by the strongly basic DMSO molecules.

Unsurprisingly the bases are among the very strongest hydrogen bond acceptors that have been studied and formation of the initial hydrogen bonds, in very dilute solutions of D_2O, are almost quantitative. More surprisingly, subsequent hydrogen bond formation only occurs at relatively high D_2O concentrations. Analyses of the infrared spectra provide a quantitative measure of the extent of hydrogen bonding to the bases as a function of solvent composition.

Acid mine drainage (AMD) elemental total concentration reduction by biological apatites

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S. Domingos abandoned copper mine, SE Portugal, is located in the Iberian Pyrite Belt. Mining activities were concentrated in the As, Cu, Pb and Zn rich sulphide orebodies. As a result of the intense mining activity is still visible a large negative environmental impact along the S. Domingos stream valley, where different type of materials, such as metallurgical slags, sub-grade ore, pyrite ash, gossan materials, and weathered host rock were deposited. Mineralogical and chemical characterization of the S. Domingos waste materials showed that most of them present potential for AMD generation resulting in superficial waters contamination.

Two samples of water were collected in the stream of S. Domingos. These waters have initial pH 2.5, conductivity 2.3 mS/cm at 287 K, redox potential 530 mV, total dissolved sulphate 1.4 g/L, and high total concentrations for Al, As, Ca, Cu, Fe, Mg, Mn, P and Pb. To reduce their total concentration in the waters, three slightly different reactors containing well-defined portions of sand, manganese dioxide sintered together with cow femoral bone chips at 823 K, synthesized pyromorphite, small pieces of the cow bones calcined at 773 and 1273 K, and limestone were assembled in columns. The water percolating through the columns was collected, and each 10 L of collected water was homogenized and analysed for pH, conductivity, redox potential, sulphate concentration, and the concentration of the elements under study.

Total concentrations of the elements Al, As, Ca, Cu, Fe, Mg, Mn, P and Pb were determined by ICP-MS, and sulphates by a gravimetric method.

The X-ray diffraction analyses of the column solids, after the percolation of 170 L of water, showed the presence of minerals such as gypsum, goethite, mimetite, and manganese arsenates. The manganese arsenates must result from the redox process between As(III) and manganese dioxide. The total concentrations in the waters collected from the columns reflect possible equilibria with the secondary solid phases.

The proposed method using biological apatite for removal of the above referred elements from the water stream was efficient. The concentrations of all the species in the final waters decreased to levels lower than the guide values presented in the Portuguese laws for drinkable water.

The experimental data will be presented and the behaviour of the system water-solid in the columns will be discussed in terms of the solubility of the identified solids under the water composition.

Hydrated Electrons in Clusters, on Interfaces, and in the Bulk

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The presence of charged species at interfaces plays a central role in a wide range of physical processes. Heterogeneous electron transfer is among the most notable examples with implications in electrochemistry, atmospheric chemistry, heterogeneous catalysis, or from a more general viewpoint, in biological through-space electron transfer reactions. An excess electron in an aqueous environment may be considered as a useful model for studying key energetic, structural and dynamic aspects of these complex phenomena. Excess electrons are known to stabilize in bulk water, as hydrated electrons. Hydrated electron systems with reduced dimensionality, such as negatively charged, finite size water clusters, and excess electrons at aqueous interfaces of infinite size, have also been studied for a while.

In the present work we will overview the results of a series of mixed quantum-classical molecular dynamics simulations aimed to examine the physical properties of various aqueous excess electron systems. The investigated systems include finite size water cluster anions, infinite ambient water/air, supercooled water/air, Ih ice/air, amorphous ice/air interfaces, and the fully hydrated electron. The discussion will focus on the critical issue whether the excess electron localizes in interior-bound states completely surrounded by water molecules, or on the water surface (interface) with significant electronic amplitude appearing outside the molecular frame (surface-bound states). Correlations of the excess electron state with the size, internal energy, and the local molecular structure of the environment will be illustrated. We will also demonstrate the dramatic influence of the excess electron state on the observable physical properties. The possible interconnections of the finite size cluster anions, the electrons at the infinite size water/air interfaces, and the three-dimensional, fully hydrated electron are also explored in comparison with available experimental data.

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A problem of molecular theories of solutions: Can we predict correctly the properties of water-alcohol mixtures by computer simulations?

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Aqueous solutions of alcohols are ones of the simplest aqueous solutions with the solute having both a hydrophilic head and hydrophobic tail. A large number of simulation results have been published for water-alcohol mixtures, focusing primarily on the structure. Available data for the thermodynamic properties (i) exhibit a very large scatter and are not in mutual agreement, and (ii) none of them predicts the most distinct feature of these mixtures, a minimum of the partial molar volume at low concentration range of alcohols.

In order to use molecular simulations, intermolecular potential models are required. However, they are available only for pure fluids. Consequently, certain combining rules must be used, typically the Lorentz-Berthelot (LB) ones. No satisfactory agreement with experiment can be achieved unless certain deviations from the LB rules are applied. Recent studies on mixtures of realistic fluid models have shown that it is a deviation from the Lorentz rule for the size parameter which may lead to a qualitative change in the behavior of the mixture. On top of this, the use of pure fluid potential models themselves for mixtures must be questioned.

One possibility to account more appropriately for the cross interactions is to include polarizability. It has been shown recently that polarizable models bring results to at least qualitative agreement with experimental data but at the expense of considerably increased complexity and CPU time demands. An alternative is to maintain the pure fluid pair-wise additivity and to develop certain rules for the combining rules. It turns out that also this route may change, qualitatively, the properties of mixtures. Nonetheless, large discrepancies between results obtained for excess properties of the same mixture using different force fields indicate that good performance for pure fluids need not be sufficient for a good description of mixtures.

All these findings will be presented and discussed along with an attempt to identify defects in pure fluid models when applied to mixtures. A potential development in this field and short-term problems to be solved will also be outlined.

Thermodynamics of hard-sphere fluids confined in random porous media studied by scaled particle theory and computer simulations.

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Despite the quite large number of theoretical investigations devoted to fluids confined in random porous media, analytical results for any non trivial off-lattice model are still lacking. In sharp contrast with the bulk fluid, no analytical results have ever been published even for a simple model like a hard-sphere fluid in a hard-sphere matrix. In this report, we present our results on extending the scaled particle theory (SPT) for obtaining the analytical expressions for the chemical potentials and equation of state of a hard-sphere fluid in Madden-Glandt models of hard-sphere and overlapping hard-sphere matrices. The developed approach is based on the combination of the exact treatment of point scaled particle in hard-sphere fluid confined in porous media with the thermodynamic consideration of finite-size scaled particle [1]. An empirical correction to the SPT was found which leads to a highly accurate expression for chemical potential over the whole density range with errors comparable to the computer simulation results. The different schemes of Carnahan-Starling improvement are analyzed. The possibilities of mapping thermodynamic properties of hard-sphere fluids in different models of porous media are discussed. This investigation is made through a careful analysis of the results obtained from grand-canonical Monte-Carlo simulations for hard-sphere fluids in overlapping hard-sphere and hard sponge matrices [2]. It is shown that thermodynamics in both models is nearly identical if the porosity of the porous materials and the mean interface area are set to be equal.

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Coarse-graining in electrolyte solutions: toward a simple but molecular description of ion specific effects

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Since the pioneering works of Debye, Huckel, and Onsager, electrolyte solutions are commonly described by continuous solvent descriptions. Ions are represented by simple models, such as the Primitive Model (PM) for which they are assimilated to charged hard spheres. These simples descriptions are especially interesting for chemical engineering because they yield explicit formula. The molecular structure of the solvent is ignored, though and consequently they cannot take proper account of complex specific (Hofmeister) effects which appear in numerous biological, chemical, and physical interfacial phenomena.
An alternative procedure consist in carying out molecular simulations. Coarse-grained desciption of ions can be obtained by averaging rigourously over the solvent configurations. In that case, many complex effects can me modelled, but the simplicity of the original aproach of Debye and Huckel is lost. This molecular description requires a numerical solution.
In order to bridge the gap between the two levels of descriptions, we propose a new approach which takes into account the molecular aspects but it provides an explicit description of the thermodynamics and the structure for ion properties in electrolyte solutions. The first stage consists in calculating the ion-ion interactions from molecular simulations, by generalyzing a procedure introduced by Lyubarchev and Laaksonen. In the second stage, Perturbative Fluid Theory is performed in order to deduce the best simple soluble models of electrolyte solutions which represent this molecular description. With the help of the MSA (Mean Spherical Approximation) and the Binding MSA (BIMSA), the final model is completely analytical and it leads to explicit formula.
The method has been applied to simple electrolytes. The advantage of such an approach is the fact that it allows the calculation the structure (g(r)) of the solutions. It can be adapted to any molecular descriptions (polarizable models, Car-Parrinello ab initio molecular dynamics, etc) as long as the statistics of the molecular simulations is enough to extract the ion-ion pair correlation functions.

Conformational Analysis of the Microsolvation of [Li+.(12C4)], [Na+.(15C5)] and [K+.(18C6)] Complexes: Ab Initio Molecular Orbital Studies

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The structure of microsolvation of some crown ethers to bind a cation was analyzed based on computational chemistry calculations using ab initio molecular orbital theory using 6-31G* basis set. The complexes of crown ether:cation were modeled as crown ether:cation, crown ether:cation:H2O and crown ether:cation:2H2O complexes. The binding energy of the complexes has been analyzed to identify contributions from structural changes and pair-wise interactions. Interactions of crown ether and cation were discussed in term of the structure parameter of crown ether, atomic charges and interaction energy of the crown ether-metals cation. The effect of substituents of -OCH3, -CH3, -Br, COOH, -CHO, -COOC2H5, and -CH=CHCO2H, on [Li+.(Bz12C4)], [Na+.(Bz15C5)] and [K+.Bz(18C6)] complexes to the selectivity of crown ethers to bind cation were studied base on ab initio molecular orbital theory calculations. Electron donating groups increase the capability of crown ether to bind cation by means of induction effect, while electron withdrawing groups reduce the ability of crown ether to bind cation. Any substituent on the benzene in crown ether which can be make the symmetrical form of the crown ether-metals cation complexes will increase the selectivity of the crown ether to bind the cation.

Molecular Level Properties of the Water-Dichloromethane Liquid/Liquid Interface, as seen from a theoretical investigation

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The understanding of the behavior of interfacial molecules at the liquid/liquid interface is indispensable from the points of view of e.g., heterogeneous catalysis, liquid chromatography, and liquid-liquid extraction. Computer simulation techniques proved to be very useful tools for this purpose, since the atomistic details of the phenomena can directly be observed. A new method (the so called ITIM method), designed to identify the truly interfacial molecules, has recently been developed by us.

To the best of our knowledge, no study has analyzed the intrinsic properties of subsurface layers of a liquid/liquid interface. Here we present a detailed analysis of the water-dichloromethane (DCM) interface by means of the novel ITIM method. We focus our interest on two particular problems, namely that (i) how deeply (in terms of molecular layers) the vicinity of the interface influences the properties of the two phases, and (ii) what is the relation of the two intrinsic surfaces covering the two phases.

Our results clearly reveal that the properties of the first molecular layer are considerably different from those of the subsequent layers in various respects. Further, in these respects the second and third layers turned out to be almost identical to each other. Thus, in both phases, the molecular scale roughness of the first layer is larger than that of the subsequent layers, and the molecules stay considerably longer in the first than in the second or third layer. Further, in water the orientational preferences of the molecules relative to the interface vanish beyond the first layer, and the two-dimensional lateral percolation network of the water molecules is only present in the first molecular layer, as well. The preferred orientations of DCM molecules are controlled by forming the optimal water-DCM interactions. The stability of the found structures are clearly supported by quantum chemical calculations performed at the B3LYP(6-31+G*) level of theory.

The surface layers of the two liquid phases are found not to be closely packed to each other. This observed loose interfacial packing, together with the different roughness of the two surface layers, suggest that the shape of the two surfaces are largely independent of each other; at some points they get close to each other, allowing, probably, even close packing at these particular positions, whereas at other parts there might be even rather large voids between the two phases.

Source of Drug Resistance: From 2004 H5N1 to 2009 H1N1 Influenza Viruses

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The outbreaks of the 2004 H5N1 and 2009 H1N1 influenza viruses have raised a concern of the global flu epidemic. To provide detailed information at the molecular level in terms of drug-target interaction, structure, solvation, dynamic and thermodynamics properties of the three known-neuraminidase inhibitors, oseltamivir, zanamivir and peramivir, embedded in the catalytic site of neuraminidase subtype N1 of both H5N1 and H1N1 viruses were studied using molecular dynamics simulations covering both wild and mutant types. For the 2004 H5N1 wild-type complexes, rotations of the NHAc and $OCHEt_2$ groups of the oseltamivir which leads consequently to the rearrangements of the NAs cavity, is a primary source of the lower susceptibility of the oseltamivir to neuraminidase subtype N1 than those in the other subtypes. In contrast with a previous proposal, the H274Y mutation does not prevent the formation of the hydrophobic pocket for the oseltamivir bulky group. Instead, reduction of the hydrophobicity and size of pocket in the area around an ethyl moiety at this bulky group were found to be the source of the oseltamivir-resistance. For the 2009 H1N1 influenza, the virus was predicted to be susceptible to oseltamivir, with all the important interactions with the NA binding residues being well conserved. In addition, oseltamivir efficiency against the probable H1N1-2009 mutants was predicted in according with the ordering of binding free energies: wild-type > N294S > H274Y > E119V > R292K. The results suggest that the H1N1-2009 influenza with R292K substitution perhaps conferred a high level of oseltamivir resistance, whilst the other mutants revealed moderate resistance levels. This result calls for an urgent need to develop new potent anti-influenza agents against the next pandemic of potentially higher oseltamivir-resistant H1N1-2009 influenza.

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Azeotropy of Alcohol-Water Binary Mixtures from the Viewpoint of Microscopic Structures

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Many alcohol-water binary mixtures show azeotropy. At the azeotropic composition, the vapor has the same composition as the liquid. We have found out that the formation of azeotrope is led by the change of evaporation property caused by the change of microscopic structures in the binary mixtures as the alcohol-water mixing ratio varies. As azeotropic mixtures, here we focus on ethanol-water, 1-propanol-water and 1-butanol-water binary mixtures.

According to the vapour-liquid equilibrium, the vapors of the boiling mixtures with lower alcohol contents are richer in alcohol in comparison with the liquid compositions. On the contrary, the vapors of the boiling mixtures with higher alcohol contents are richer in water. Such evaporation property change leads to the formation of azeotrope at a certain mixing ratio.

The microscopic structures were studied through mass spectrometric analyses of clusters isolated from liquid droplets. In the low-alcohol content (3 wt%), the observed clusters were mainly composed of hydrogen-bonded water molecules, and alcohol molecules had hydrogen-bonding interactions with the water clusters. These hydrogen bonds between the alcohol molecules and the water clusters decomposed with an increase of the temperature. On the other hand, in the high alcohol content (96 wt%), the observed clusters were mainly composed of hydrogen-bonded alcohol molecules, and water molecules had hydrogen-bonding interactions with the alcohol clusters. These hydrogen bonds between the alcohol clusters and the water molecules decomposed with an increase of the temperature.

The observed temperature effect on the cluster structures has a good correlation with the vapor-liquid equilibrium. Here we report that the azeotropy of alcohol-water mixtures is attributed to the cluster structure in the liquid state which controls volatility of alcohol and water.

On the Molecular Origin of the Nano-Segregated Structure of Ionic Liquids

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Room temperature ionic liquids are essentially mixtures of cation and anion, and solvation by such a mixed solvent strongly depends on the solvent liquid structure, particularly its miscibility. Therefore, for deeper understanding of the solvation by ionic liquids, it is indispensable to reveal their liquid structure at a molecular level.

Recently, Pádua and Lopes et al. have shown the nano-segregated structure of 1-alkyl-3-methyl-imidazolium based ionic liquids; i.e., ionic liquids are consisted of the nano scale ionic and hydrophobic domains.[1] According to small angle X-ray scattering experiments by Triolo et al., unique peaks appeared at a small *Q* (a scattering vector) region (hereafter, we call it pre-peak), and their position and intensity shifted towards a smaller *Q* side and was enhanced with increasing an alkyl chain length, respectively.[2] They ascribed the pre-peak to the nano-segregated structure, probably an alkyl chain aggregation of ionic liquids. Moreover, Atkin and Warr found that the pre-peak appeared in small angle neutron scattering patterns of ethylammonium nitrate and propylammonium nitrate ionic liquids.[3] We also found the terminal methyl groups among the cations significantly correlate with each other in ethylammonium nitrate.[4]

Here, we have new questions; *what is molecular origin of the nano-segregated structure of ionic liquids and how does it operate?* In order to answer such questions, we performed high-energy X-ray diffraction (HEXRD) experiments for 16 ionic liquids. In this presentation, we report that the nano-segregated structure is remarkably enhanced in protic ionic liquids. In particular, the pre-peak for a primary hexylammonium ionic liquid yields rather higher intensity relative to that for a 1-hexylimidazolium one, which suggests that entropic excluded volume effect certainly operates in the nano-segregation. The experimental evidences clearly indicate that molecular origin of the nano-segregation of ionic liquids is ascribed to an auto-solvophobic property of RTILs themselves.

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Interaction of chiral compounds in polar and non polar solution at 298.15 K

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Enantiomers are unique molecules that have extensive effects throughout several aspects of chemistry, biology and pharmacology. While difference of hetero-chiral compounds was discussed qualitatively, were not defined quantitatively. Hence physicochemical studies of model compounds in solutions are fundamental important for understanding the different aspects of chiral compounds. In order to clarify the molecular interactions between enantiomers of dicarboxylic acids, camphor and its derivatives in ethanol solution were determined in dilute concentration. In this work, to clarify the effect of solvation, excess enthalpies HE of non-polar chiral limonene and polar fenchone in polar and non polar solvents were determined over the whole range of concentrations at 298.15 K. Also the results were compared with quantum chemical prediction. HE was determined by twin-microcalorimeter at 298.15 K. To estimate physicochemical properties of chiral compounds, and molecular interaction in solvents were carried out by the Gaussian programs 03 at the MP2/6-311G(d,p) level of theory. The experimental results for HE of chiral compound of limonene or fenchone and solvents of ethanol, hexane, cyclohexane and benzene showed negligible small and endothermic reaction whole range of mole fraction. However those of carbon tetrachloride showed exothermic. The experimental results for HE of R-enantiomer and S-enantiomer in solutions showed exothermic unique behavior. For limonene systems, HE showed exothermic behavior in low concentration. However enthalpic stabilization decreased with increasing the concentration of limonene. And finally HE showed slightly endothermic behavior. For fenchone systems, HE showed small exothermic behavior and stabilization decreased with increasing the concentration. To clarify these enthalpies behavior of concentrations, HE of hetero chiral compounds in the solvents at equimolar concentration of enantiomers were investigated. The concentration dependences of limonene systems were similar as dicarboxylic acids and camphor and its derivatives but that of fenchone were different. So chiral oriented solvents in the solution might be interaction each other by mixing and change the solvation state to make more stable solution. The results of quantum chemical calculation will be compared with experimental results and discussed.

Isobaric Solubility and Liquid–Liquid Equilibrium Measurements of 2,2,2-Trifluoroethanol with Cyclohexane and 2-Propanol at T = (288.15, 298.15, 308.15) K

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A study to attain the solubility and liquid-liquid equilibrium (LLE) data for the ternary mixtures of (cyclohexane + 2-propanol + 2,2,2-trifluoroethanol) was carried out at temperatures of (288.15, 298.15, 308.1) K and pressure 101.2 kPa. Solubility data were obtained by titration and LLE by gas-liquid chromatography.
The consistency of the binodal curves and phase diagram data were well tested by Hand and Othmer-Tobias empirical equations. The reduced binary interaction parameters by NRTL and UNIQUAC thermodynamic models were shown to yield accurate values for the LLE of the three systems. Also the thermodynamic models correlated successfully the plait points, distribution coefficients, and solvent selectivity. The immiscibility region of the ternary mixtures decreases significantly with increasing temperature.
This work outlines the high efficiency of liquid extraction using 2-propanol as solvent to yield pure 2,2,2-trifluoroethanol at ambient temperature.

Dynamics of water and ions in clays - neutron scattering and microscopic simulation

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Clays are layered alluminosilicates with water retention and ion exchange properties, which are responsible for many natural phenomena such as retention of molecules by soil and exploited in the many technological applications of clays, e.g. in catalysis and radioactive waste disposal. We deal with the microscopic structure and motion of water and cations (Na^+ and Cs^+) in clays, as a function of clay hydration. At low clay hydration, water and cations in clays are found in a quasi two-dimensional (2D) confinement between individual, negatively charged clay layers and at very high ionic concentrations (order of 10 water molecules per ion).

Using the examples of a natural montmorillonite clay and a synthetic hectorite clay we present a comparison of experimental (quasi-elastic neutron scattering) and simulated (classical Molecular Dynamics) dynamic data. These agree in the diffusion coefficient of water confined in clay, predicting its decrease by a factor of 10 and 3 with respect to bulk water, when a single and a double water layer is confined between clay layers respectively [1].

Simulation points to very different modes of diffusion for the two ions considered: a clear jump diffusion is seen between preferential adsorption sites on the clay surface for Cs^+ ions, a more diffuse motion is observed for Na^+ ions. At the same time, their diffusion coefficients are similar, of the order of 10^{-10} m^2s^{-1}. The 2D nature of water and ion diffusion is clearly seen in simulation, it is obscured in neutron scattering data due to the use of powder clay samples. It can be revealed, using a novel method based on analyzing the scattered intensity at zero energy transfers at a wide range of energy resolutions [2].

Lastly, we consider the exchange of ions between the interlayer, microscopic porosity of clays and a bulk aqueous solution. The calculation of the potential of mean force (PMF) for an ion entering the clay interlayer from the bulk solution reveals an energetic barrier only for negatively charged ions, supporting the experimentally observed anion exclusion from low hydrated clays [3].

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Density fluctuations and local structures in aqueous solutions from x-ray spectroscopy and x-ray scattering measurements

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Ions are traditionally categorized into structure-breakers and structure-makers based on the strength of their interaction with water. However, this classification is ambiguous and based on macroscopic properties, offering no structural details of the water-ion interaction. We have recently obtained new experimental data on water using various x-ray spectroscopic and x-ray scattering tools, which have been interpreted based on a fluctuating hydrogen bonding (H-bonding) network around a bimodal distribution of local structures; distorted H-bonded and tetrahedral [1]. These can be linked to the discussion of a second critical point in supercooled water in terms of high density liquid (HDL) and low density liquid (LDL) [2]. The question is how do ions affect the fluctuating H-bonding network and can the structure breaker and maker concept be aligned with the occurrence with HDL and LDL structures for aqueous solutions.

Using small angle x-ray scattering (SAXS) and x-ray absorption spectroscopy (XAS), we compare the effect of increasing cation valency on the structure of water, such as NaCl, $MgCl_2$, and $AlCl_3$ solutions, and changing anions between F^- and Cl^-. From our data, we offer an interpretation of structure breaking and structure making properties of ions in terms of density fluctuations and the ability to form various hydration shells. Di- and trivalent ions with strong hydration shells that do not participate in density fluctuations can be considered as structure makers. On the other hand, monovalent ions that do not have well defined hydration shell and shift the density fluctuations towards HDL can be considered as structure breakers.

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Structure Determination of Hydrated and Hydrolyzed Thorium (IV) Ions in Solution

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The structures of hydrated and hydrolyzed thorium(IV) complexes in aqueous solution at different pH values have been investigated by EXAFS and LAXS. It has been shown that in strong acidic solution (pH=0), the thorium(IV) ion is hydrated by 9 water molecules in tricapped trigonal prismatic configuration in the first hydration sphere at mean Th-O distance of 2.46 Å, and by ca. 18 water molecules in the second coordination sphere at 4.65 Å.

It has been shown from potentiometric investigations that the first hydrolysis complex, $[ThOH]^{3+}$ easily dimerize, and the second complex, $[Th(OH)_2]^{2+}$ forms tetramers or hexamers, and that further hydrolysis results in hexamers with composition $[Th_6(OH)_{14}]^{10+}$ and $[Th_6(OH)_{15}]^{9+}$[1]. Our studies show that in the dimer the thorium(IV) ions are connected by a double hydroxo bridge and each thorium binds additionally six water molecules, see Figure below. The thorium(IV) ions in the tetramer are connected by double hydroxo bridges with the same Th•••Th distance as in the dimer, and with four terminal water molecules on each thorium giving a composition of $[Th_4(OH)_8(H_2O)_{16}]^{8+}$, see Figure below. The thorium(IV) ions in the tetramer form a diamond with Th•••Th diagonal distances of 4.7 and 6.6 Å.

The hexamer has slightly longer Th-O distances, 2.40 Å, than in the dimer and tetramer, and with the same diagonal Th•••Th distances but in larger numbers strongly indicating a rhomboctahedral structure of the thorium(IV) ions. In such a structure there is not room for 14-16 hydroxide groups, and instead the eight hydroxo groups have been converted to oxo groups bound to thorium ions giving a complex with composition, $[Th_6O_8(H_2O)_{16}]^{8+}$, where each thorium(IV) ion binds to four oxo groups and four terminal water molecules.

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Kinetics of proton transfer in aqueous systems of varying dimensions

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We will discuss various structural and dynamical aspects of protonic defects in aqueous systems by means of ab initio molecular dynamics[1], combined quantum-classical molecular dynamics[2] and and population correlation function[3] approaches. In particular, we will focus on the proton transfer kinetics in aqueous systems having an excess proton and also a proton less and we will correlate the observed kinetics to the solvation structure of the charge defect and also to the kinetics of hydrogen bond fluctuations in the surroundings. We have considered aqueous systems of different dimensions such as water clusters of different sizes[4], a monolayer of water molecules confined between two graphite plates and one-dimensional water chains confined in carbon nanotubes of different lengths. The kinetics and mechanism of proton transfer in lower dimensional systems are compared with those of bulk aqueous solutions. Also, the connections of the present results to those of recent ultrafast spectroscopic studies are discussed.

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Studies on Ionic Conductance of Solution Complexes of Some 3d-Metal Ions

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Electrolytic conductivity is the measure of the mobility of the ions present in the solution. The ionic mobility in turn depends on the charge and the size of the metal ions and their interaction with the solvent molecules. When the metal ions form a complex with the solvent molecules or some other ligand, its conductivity is reduced. Hence, the conductance may be considered as a reasonable tool to predict the formation and stability of complexes in solution.

In the present study, the electrolytic conductance of Nickel(II), Copper(II) and Zinc(II) ions have been investigated in the aqueous medium as well as in 1M Sulphuric acid, 1M Acetic acid and 1M Ammonia. The binary complexes of Nickel(II), Copper(II) and Zinc(II)) with L-glycine, L-serine, L-cysteine, L-glutamic acid, L-histidine and L-tyrosine were synthesized. The ionic conductances of these complexes in all the four mediums were studied. Cu(II) ion shows lowest conductance in all the mediums indicating it forms stable complexes. The conductivity of the Metal(II)-amino acid complexes shows much lower values than those of the free metal ions, which shows that these solution complexes are quite stable. The conductivities of these complexes in the four mediums are compared and they show very high conductance in 1M sulphuric acid medium than the other three. This indicates that in this medium, the solvent molecules are not involved in complexation and the stability of the complexes is also comparatively lower. In all the systems investigated, the conductivity sharply increases below 0.04M concentration. Hence we can assume that the complexes begin to dissociate below this concentration.

Molecular dynamics simulations of ethanol-carbon dioxide mixtures along the liquid vapor coexistence curve

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Supercritical CO_2 and CO_2-expanded liquids (CXLs) are the alternate media for performing chemical reactions. Expanded liquids combine the beneficial properties of compressed CO_2 and of traditional solvents, leading to a new class of tunable solvents that are often the ideal type of solvents for a given application while simultaneously reducing the environmental burden. Supercritical CO_2-expanded ethanol is an advanced medium for high selective extraction possesses, formation of nanoparticles, nanofilms, and membranes.

Molecular dynamics simulations have been performed for carbon dioxide - ethanol along the experimental liquid vapor coexistence curve: two for the pure components and nine for the mixtures, containing 0.1-0.9 mole fraction x_2 of ethanol. MD simulation was carried out using the DL_POLY program in a *NPT* ensemble at T=313K. The Zhang and Chen potential models have been used for CO_2 and ethanol, respectively.

The compositions and densities of the liquid phases of the binary system at equilibrium are critically compared with corresponding literature values. A satisfactory agreement was obtained between experimental and calculated phase compositions and saturated densities.

Structural properties of the mixture were investigated through the radial distribution functions (RDF), hydrogen bond network properties and the statistical geometry approach. H-bond analysis and dipole correlation functions show that the local geometry of the H-bonded ethanol molecules remains nearly unchanged with varying composition of the mixture. The ethanol molecules form the ramified chains in supercritical mixture even at 0.1 mole fraction of ethanol. The solute-solvent structure reorganization and preferential solvation of the mixture components are discussed in terms the local mole fractions of the *i* component molecule around a reference molecule of the *j* component x_{ij}^{loc}.

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First determination of successive complexation constants in a ionic liquid: The UO_2^{2+}/NO_3^- system in C_4-mimTf_2N as studied by UV-vis and chemometric methods

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Ionic liquids (ILs), are a new class of solvents, composed of an (in)organic cation (most frequently : imidazolium, pyrrolidinium, tetraalkylammonium...) and an inorganic anion (PF_6^-, BF_4^-, Cl^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$ etc), with so many industrially beneficial properties (in particular, ILs are non flammable and non volatile thus being often called green solvents) that an increasing number of publications is devoted to their study as replacement solvents in all fields of chemistry (electrochemistry, catalysis, synthesis, liquid/liquid extraction etc). Some very fundamental or basic chemical aspects are also covered, such as solvation, complexation or extraction mechanism of various ions or molecules in ILs. ILs also represent a real challenge for theoreticians, because of their intrinsic (chemical) complexity. At the same time, ILs offer a unique chemical media to test correction laws (either empirical or analytical) for activity coefficients at very high ionic strength. Surprisingly enough, however, very few papers are concerned with the determination of equilibrium chemical constants in ILs, which is a prerequisite to the study of ionic strength effects and coulombic interactions in ILs.

Our group is interested in actinide and lanthanide chemistry in ILs, both on fundamental and applied aspects. We intended to experimentally derive the equilibrium constants of UO_2^{2+} with NO_3^- in a classical IL, 1-methyl-3-butylimidazolium bis(trifluorosulfonyl)imide (denoted as C_4-mimTf_2N, Tf_2N- standing for the $CF_3(SO_2)_2N^-$ anion and C_4-mim^+ being the imidazolium based cation). UO_2^{2+} has been chosen as the reacting cation, based on its well-defined UV-vis spectra and amount of literature data on complexation in various solvents by UV-vis spectroscopy, that can be used for comparison purposes. We selected the NO_3^- ligand, leading to a limiting complex of 1:3 stoechiometry only, which is of interest to studies related to the nuclear fuel cycle and has already been studied in C_4-mimTf_2N. The UV-visible data and the values of the derived conditionnal constants will be presented and discussed under the light of two models for the complexation sequence, that have been treated with basic chemometric methods.

STATIC DIELECTRIC CONSTANT AND WATER ACTIVITY OF CONCENTRATED ELECTROLYTE SOLUTIONS

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The static dielectric constant (ε_s) determines the electrostatic part of hydration processes. In the concentrated solutions of salts ε_s is not equal to dielectric permittivity of pure water which enters into many theoretical equations for calculation of activity coefficients, constants of equilibrium and other thermodynamic characteristics (Debye-Huckel, Pitzer equations etc.). The measurements of ε_s in salt solutions are impossible because of their high conductivity. However, now we can calculate ε_s from high frequency dielectric data. The experimental method of microwave dielectric spectroscopy (7-25 or 7-120 GHz) was advanced for ε_s determination of concentrated electrolyte solutions in the temperature range. Systematic research of complex dielectric permittivity and low-frequency conductivity for 50 binary and multicomponent water-electrolyte systems was carried out. Its ε_s were calculated. The general systematization of aqueous electrolyte solutions was developed according this parameter. It includes the data of high concentrated, saturated and oversaturated solutions for binary and ternary systems. Their comparison with ε_s for solutions of acids and the bases was carried out. It has been established experimentally: 1) the significant differences of values and dependences ε_s in various concentration ranges (in the concentrated solutions ε_s =20-30) and the practical absence of ε_s changes in high concentrated solutions; 2) the correlation of ε_s and complex formation in solutions (on the data of electronic spectra) and unusual order of ε_s changes with the variations of ion charge and radius in this cases; 3) the features of ε_s changes, appearing at the transition from binary to ternary systems (in particular the ε_s values practically do not vary in concentration area where the crystallization of double salts is observed).
The relationships of concentration changes of water activity (a_w) and ε_s of the concentrated salts solutions were investigated. The linear character of a_w dependence on $1/\varepsilon_s$ was shown at 298 K (20 binary systems). The concentration limit of the first structural zone of solutions where this dependence is observed was established. The obtained dependences were used for calculation and analysis of concentration changes of osmotic coefficients, coefficients of water activity and other properties of the solutions.
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The Liquid-Liquid Phase Transition in Solutions of Ionic Liquids

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Because of the high melting points of inorganic salts liquid-liquid phase transitions in ionic solutions could be observed on very few systems only [1] till recently. Now, a great number of rather stable organic salts with melting points below 100°C, termed ionic liquids, became available, and a substantial number of ionic solutions has been discovered that have a critical point at ambient temperatures. Thus systematic investigations of the critical properties and corresponding state analysis [2] became feasible. Here we report phase diagrams of solutions of alkyl-methylimidazolium trifluormethylsulfonates (Cnmim-triflat) in haloarenes (Chlorobenzen, Bromobenzene, Jodbenzene), alcohols, dioxane, and water and alkyl-methyl imidazolium bistrifluormethylsulfonylimides (CnmimNTF2) in hydrocarbons and alcohols and compare with solutions of other salts. The systems have an upper critical solution point and the phase diagrams are consistent with the presumption of Ising critical behavior.

A corresponding state analysis is carried out using as a reference the so called restricted primitive model (RPM), which considers charged hard spheres in a dielectric continuum. Using the corresponding-state variables of this model general agreement for the location of the critical point with the RPM prediction is found for solutions in non-polar solvents. The critical temperatures (in the RPM-scale) of the solutions in polar as well as in non-polar solvents including hydrocarbons and polar solvents (including water) vary linearly with the dielectric permittivity of the solvents. The critical compositions and the shape of the coexistence curves are different for solutions in aprotic (alkanes, arenes) and protic solvents (alcohols, water). In the RPM temperature scale the critical points in the aprotic solvents are upper critical points, while in protic solvents the critical points become lower critical points [2], which indicates that in protic solvents the Coulomb interactions and the breaking of hydrogen bonds both are the driving forces of the phase transition. No systematic is observed within one of the two groups when comparing the widths as well as the slopes of the phase diagrams in the corresponding state representation.

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Transport coefficients : a path to explorate colloidal and polyelectrolyte solutions

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Transport coefficients such as electrical mobilities or diffusion coefficients can be measured on a collective or on an individual basis; bulk electrolyte or single ion conductivities, collective or individual diffusion coefficients.
We determine transport coefficients of different colloidal and micellar systems, as well as natural polyelectrolytes such as soil natural organic matter, by several experimental methods: electrical conductance, electrophoretic mobilities (optic and acoustic zetammetry), diffusion coefficients: individual by NMR, collective by dynamic light scatteriing.
The results can be compared to the predictions of different mesoscopic theoretical models, such as MSA dynamic and brownian dynamics. In any case counterion condensation is a major factor which has to be taken in to account for a proper quantitave decription of the system.

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Alkyl-chain dependence on the liquid structure of 1-Alkyl-3-methylimidazolium based room-temperature ionic liquids

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Room-temperature ionic liquids (RTILs) are widely applied to chemical reactions and processes and electrochemical devices etc. as replacements for conventional molecular solvents. An understanding of physicochemical properties has also been advanced in recent years, i.e., thermodynamics, dynamics and structure of RTIL have been reported by experimental and theoretical techniques. It has been reported by MD simulations that RTILs with long or intermediate alkyl-chain length are not homogeneous in the liquid state and are highly structured at nano-scale level to form a nonpolar (alkyl-chain aggregation) and a polar (charged part of cation and anion) domains.[1] The nano-segregation in RTILs has been confirmed by small-angle X-ray scattering (SAXS) experiments.[2] However, the evidence of the nano-segregation in RTIL is not enough at the present stage, i.e., it is not established what structure or interaction at nano-scale level corresponds to the scattering peak observed by SAXS or SANS. In this work, SANS measurements were made on 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, C*n*mim$^+$TFSA$^-$ ionic liquids with the alkyl-chain length, n = 2 - 12, and also on the deuterated ionic liquids, Cn(D)mim$^+$TFSA$^-$ where H atoms in the alkyl-chain group are replaced by D atoms.

SANS peak observed for the deuterated C*n*(D)mim$^+$TFSA$^-$ intensified with increasing n and the peak position shifted to a lower Q side. These SANS profiles were subtracted by those for the corresponding normal ionic liquids to obtain difference SANS profiles, $\Delta I(Q)$ (= $I(Q)_{[Cn(D)mimTFSA]}$ - $I(Q)_{[CnmimTFSA]}$). The obtained $\Delta I(Q)$ showed no peak over the whole Q range examined. This strongly suggests that the peak in the SANS profile is not ascribed to the scatterings from the alkyl-chain of the cation, i.e., contributions from alkyl-chain...alkyl-chain, alkyl-chain...imidazolium ring and alkyl-chain...TFSA correlations are very small on the observed scatterings. The observed SANS peak should be assigned to the contribution other than above correlations, it is the TFSA...TFSA correlation at long-range scale. This conclusion is indeed supported by our MD simulations.

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Ion Association in Solutions of Imidazolium RTILs: Combining Conductivity Measurements and Dielectric Spectroscopy

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Room-temperature Ionic Liquids (RTILs), which are formed by large organic cations with a variety of anions, are intensively studied for potential applications as reaction media or for liquid-liquid extraction, with RTILs based on 1-alkyl-3-methylimidazolium cations being probably studied most. Practical applications almost inevitably involve mixtures of these compounds, either with reactants and products or/and with added co-solvents. To optimize the solvent properties of RTILs it is therefore necessary to understand their mixing behaviour. This not only requires knowledge of the pure RTILs but also information on the interactions of the constituting ions diluted in the second component.

We report the investigation of solutions of [bmim][Cl] in water and acetonitrile and of [bmim][BF_4] in acetonitrile with conductometry and dielectric spectroscopy. Precise conductivity measurements[1] in the concentration range of c_{IL} = $2*10^{-4}$- $5*10^{-3}$ M were used to determine the standard-state association constants, $K_A°$, and the molar conductivites at infinite dilution, Λ_0. From the latter the limiting ionic conductivities, λ_0, of $[bmim]^+$ in water and acetonitrile was derived. The $K_A°$ values were used to crosscheck the ion-pair concentrations determined by dielectric spectroscopy[2] for RTIL concentrations up to 4 M (x_{IL} < 0.2). Comparison of the results from both methods unambiguously revealed contact ion pairs (CIPs) as the only dipolar aggregate formed in the solutions. Analysis of the ion-pair relaxation times suggested that the rate on which CIPs form is close to diffusion controlled. With increasing c_{IL} the fraction of CIPs decreased considerably until at x_{IL} ≈ 0.2-0.3 this species could not be detected anymore. The data suggested that this was mainly due to redissociation as a consequence of increased ion-ion interactions but there were also indications, especially for the aqueous systems, for the formation of larger non-polar aggregates. At x_{IL} ≈ 0.2-0.3 the dynamics of the investigated RTIL/polar solvent mixtures transformed smoothly from electrolyte-solution-like to molten-salt-like behaviour.

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How Co-Ions Influence the Dynamics of Ionic Microemulsions A Dielectric Relaxation Study

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Microemulsions play a considerable role in current research activities from technical applications to the elucidation of biological systems. In the past years numerous investigations led to a better understanding of this field; however, some essential aspects are still unexplained.

The influence of co-ions on the system didodecyldimethylammonium bromide (DDAB) / water (W) / *n*-dodecane (D) is a typical example for this: At room temperature, a homogeneous L_2-microemulsion is formed over wide areas of the phase diagram. However, adding bromide salts to this system beyond a threshold concentration induces the shrinking of the stability region of the microemulsion to a tiny island, that remains constant against further electrolyte addition. The reason for this phenomenon is obscure, especially since the threshold concentration only amounts to 1% of the total ion concentration. As the bromide concentration in the solution remains virtually constant, it is obviously due to a cationic effect. Elucidating this phenomenon would mean a major step towards an understanding of the co-ion influence on the stability of polyelectrolyte solutions in general.

Thanks to its sensitivity to collective modes of hydrogen bond systems and the reorientation of transient dipolar aggregates dielectric relaxation spectroscopy (DRS) provides valuable information on the dynamics of cooperative processes and on the structural consequences arising from that. This method is particularly suitable for the investigation of the phenomenon described above, as it reveals characteristic polarisation relaxations caused by the ions at the W/D interface. Relaxation processes stemming from the water network in the core of the aqueous subphase and near the W/D interface, respectively, are also detected.

We have shown previously that the dielectric spectra of DDAB/W/D microemulsions can be described best by a superposition of six relaxation processes, reflecting *charge hopping*, interfacial polarisation effects, uncorrelated movements of ionic species and two types of water relaxation. In the present contribution, the influence of the co-ions lithium, sodium, caesium and tetramethyl ammonium on each of these six relaxations will be investigated. Our data strongly suggest that the co-ions are located near the W/D interface and modify its structural properties. In contrast, water dynamics are barely influenced.

Thermodynamic Study on the Autoprotolysis in a Protic Ionic Liquid, Ethylammonium Nitrate, and Its Aqueous Mixtures

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Protic ionic liquids (PILs), made from a strong acid and base, have recently received increasing attention as new proton conductors and media of acid-base reactions. Ethylammonium nitrate ($EtNH_3^+NO_3^-$, EAN) is a typical PIL in which a liquid structure is built up based on a hydrogen-bonding network to show a water-like property such as negative enthalpy and entropy of gases dissolution, micelle formation, aggregation of hydrocarbons, *etc.* We have already demonstrated the ordered liquid structure of EAN by an X-ray scattering technique and an MD simulation. On addition, an aqueous mixture of EAN is also attracting for its mutual solubility, regular manner in mixing, and the ability to dissolve alkaline phosphatase without degeneration in high EAN content. Although many physicochemical measurements were carried out in EAN-water mixture, the acid-base property has hardly focused on. Thus, we determined the thermodynamic property of autoprotolysis in the mixture directly by means of a potentiometric and calorimetric titrations. Note that the equation, $EtNH_3^+ + NO_3^- \rightarrow EtNH_2 + HNO_3$ is equivalent to autoprotolysis in an amphoteric solvent, which is the most characteristic physicochemical quantity concerning an acid-base property.

In neat EAN, both the free energy and entropy of autoprotolysis, $\Delta H_{AP}°$ and $\Delta G_{AP}°$, are large and positive. It is a similar situation to water. However, the entropy, $\Delta S_{AP}°$, is large and positive in EAN while large and negative in water. This can be explained by a different solvation state of an acid- and a base-species. That is, neutral species, $EtNH_2$ and HNO_3, are generated by autoprotolysis in EAN as an acid- and a base-species, which are less tightly solvated by ionic solvents, $EtNH_3^+$ and NO_3^-, while ions, H_3O^+ and OH^-, are generated in water, which make strong hydrogen bonding with H_2O. At the wide range in the moderate mixing ratio ($0.2 < x_{EAN} < 0.9$), $\Delta G_{AP}°$, or autoprotolysis constant, seems to be kept almost unchanged. This provides a steady acid-base environment in the mixture. However, $\Delta H_{AP}°$ and $\Delta S_{AP}°$ increase with increasing x_{EAN} and compensate each other to give constant $\Delta G_{AP}°$; this reflects the change of liquid structure in the mixture depending on the composition.

Poster Session I

Posters 100-199

ORGANIC COMPOUNDS IN ALLENDE METEORITE: AN OVERVIEW AND NEW ANALYTICAL APPROACHES

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Astrobiologically, it is important to note that carbonaceous chondrites are the closest spectral analogs available in laboratory of the carbonaceous asteroids that impacted the Earth during the Hadean eon. Carbonaceous chondrites are a primitive and undifferentiated group of meteorites, which contain organic material and provide a valuable and tangible record of the chemical steps taken towards the origin of life in the early solar system. The bulk of the organic carbon in carbonaceous chondrites is a macromolecular material containing H, N, O and S.

In addition to the recent and extremely interesting Tagish Lake carbonaceous chondrite, which fell in Canada on January 18, 2000, among the most studied carbonaceous chondrites are Orgueil (>12 kg), fell in France in 1864, Murray (around 12.6 kg), fell in the US in 1950, Allende (>2000 kg), fell in Mexico in 1969, and Murchison (>100 kg), fell in Australia in 1969. Therefore, the Allende meteorite is the largest carbonaceous chondrite ever found on Earth. The fireball was witnessed in 1969, falling over the Mexican state of Chihuahua. After breaking up in the atmosphere, an extensive search for pieces was conducted. The Allende meteorite is notable for possessing abundant, large calcium-aluminium-rich inclusions, which are among the oldest objects formed in the solar system, 4.6 billion years ago. Allende meteorite contains a 0.25 weight % of carbonaceous material. This organic material in meteorites provides insight into the cosmochemistry of the early solar system.

We have analyzed Allende for proteinaceous aminoacids and apolar hydrocarbons. In order to eliminate the possible superficial contamination, previously to the analysis, the sample was washed successively with chloroform, HCl 6N and water. We have detected a set of aminoacids: aspartic acid, glutamic acid, serine, glycine, alanine, arginine, proline, tyrosine, t-leucine, isoleucine, leucine and phenylalanine by HPLC with a photodiode array detector after acid hydrolysis of the water soluble residue. The analysis of linear and branched hydrocarbons and aromatic compounds were made in one step using SPME/GC-MS techniques. These kind of compounds have been previously detected in meteorites but not using this elegant, clean and powerful tool. Thus, we have detected aliphatic, linear and branched, hydrocarbon from C_{10} to C_{20}, alkylbencenes and polycyclic aromatics such as naphthalene.

Carbon Dioxide in water - A quantum mechanical charge field molecular dynamics study

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Characteristic features of the structure and dynamics of carbon dioxide in water have been assessed by applying the ab initio quantum mechanical charge field molecular dynamics (QMCF MD) formalism. This study was carried out at Hartree-Fock quantum mechanical level using Dunning double zeta plus polarization basis sets for C, O and H, to establish the properties of hydrated carbon dioxide. The simulations reveals that in average 10 water molecules surround the carbon dioxide molecule in the first hydration shell of 4.5 Å diameter and both oxygen of carbon dioxide equivalently form hydrogen bonds with solvent molecules. Structural parameters like radial distribution functions, angular distribution functions and coordination number distributions are employed to characterise structural features. The dynamics of hydrated carbon dioxide were evaluated by calculating mean residence time of the solvent molecules around the solute in the first hydration shell.

Structural and dynamic properties of a water monolayer on TiO2 surface: Ab initio molecular dynamics study

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Recently Boerio-Goates et al. [1] reported new synthetic methods to prepare nanoparticles of anatase and rutile (TiO2) that have exceptional purity, both in terms of phase and chemical composition, and performed calorimetric studies of rutile with varying levels of surface hydration (from water monolayer up to 4 water layers on the surface). A complexity of microscopic processes occuring at the water-rutile interface does not permit simple modeling of its structural and dynamic features using classical molecular dynamics. In recent years considerable progress has been made towards theoretical modeling of the adsorption of water on metal oxide surfaces and, in particular, on titanium dioxide TiO2(110) at low coverage [2].

We report structural and dynamical properties of water monolayer on a top of rutile (001) surface at the room temperature, studied by means of ab initio molecular dynamics (AIMD) simulations. The electronic subsystem was treated within the density functional theory with generalized gradient approximation. The effective electron-ion interactions were represented by ultrasoft pseudopotentials, which permit quite a small cut-off energy of 25 Ry. The ab initio simulations were performed with the VASP package. We report pair distribution functions and bond-angle distributions of the water molecules on the rutile (001) surface. Dynamical properties are represented by the velocity autocorrelation functions and time evolution of hydrogen bonds. We show, that one of the most interesting features in dynamics of water monolayer on rutile is a correlation in proton motion of neighbour hydrogen bonds. The time-dependent proton distribution at the water monolayer is discussed.

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Investigation of cationic and anionic hydrolysis mechanism for As(III) and arsenate ions in neutral aqueous medium.

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Ab initio QMCF MD simulation has been employed to reveal the mechanisms of ionic hydrolysis for the As(III) cation and AsO_4^{-3} anion in aqueous medium on the microscopic scale to describe ultrafast proton transfer processes taking place during the event. As(III) undrgoes rapid hydrolysis resulting in relatively stable $As(OH)_2^+$ species and the formation of hydroxonium ion.
The arsenate anion is protonated by solvent water and resulting in a hydrated OH^- ion and $HAsO_4^{-2}$. The hydrated OH^- anion undergoes further proton exchanges via a transient $H_3O_2^-$ species.

Asymmetric Hydration of Sn(II): An ab initio QMCF MD Study

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The structural properties of the hydrated Sn^{2+} ion have been investigated using ab initio quantum mechanical charge field molecular dynamics (QMCF MD) simulations at double-ξ HF quantum mechanical level. The results indicate a set of characteristics for the first hydration shell uncommon among metal ions. With the application of a spatial decomposition scheme, two different ligand binding dispositions were observed: the underlying shape of the primary hydration layer being an uneven spheriod having one end closer to the ion that the other. Consequently, the dynamics present in the two ends of the spheroid were found to exhibit different characteristics. This behavior would have been difficult to reproduce without the invocation of extensive ab initio QM treatment as provided in the QMCF MD framework.

Identification and Linkage of Ionic Species in Molten Samarium Trichloride-Alkali Chloride Systems

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Liquid structure of lanthanide trichlorides has been analyzed by X-ray diffraction or Raman spectroscopy, for instance, on pure CeCl3 with UCl3-type crystal structure [1] and ErCl3 with AlCl3-type [2]. Those results suggested that the nearest neighbor Cl- coordination number of Ce3+ ion changed from 9 in the crystal to 6 in the melt and that of Er3+ ion was unchanged to be 6 in both crystal and melt, allowing for octahedral geometry around the lanthanide ions. By analyzing the Ce3+-Ce3+ and Er3+-Er3+ distances and the volume increases on melting, there appeared to exist the corner-sharing linkage of octahedra in molten CeCl3 and the edge-sharing combination of octahedra in molten ErCl3, in a sense of "most probable type of linkage", which characterize the melting behavior of a series of lanthanide trichloride crystals [3]. A little is, however, known about the structure of molten SmCl3-ACl [A = Li, Na, and K]. In the present work Raman spectroscopy was used to identify the ionic species in the melts. Especially for SmCl3-NaCl melts the molecular dynamics simulation was applied to study the ionic arrangements and interpret the variation of Raman spectra with composition and temperature. The conclusions were obtained as follows; (i) there existed octahedral complex species $SmCl_6^{3-}$ according to Raman spectroscopy and X-ray diffraction; (ii) most of ligands Cl-'s forming the above octahedra were bound to the adjacent octahedra, that is, a common Cl- lay between the two octahedra, allowing the more complexation in the SmCl3-rich melts; (iii) Due to the phenomenon in (ii), complicated behaviors such as ν_1 peak splitting and shifting which might originate from the "polymeric" or "clustering" species occurred in vibrational modes, and the bending vibration disappeared to be practically Raman inactive in the high SmCl3 concentration range partly because of the low symmetricity of octahedra; (iv) The effect of alkali chloride addition on the octahedral structure and the linkage of octahedra were well interpreted by MD simulation, in other words, the supply of ligand Cl- to the melt led to the bond-breaking among octahedra (in the polymer or the cluster), allowing the abundance of isolated octahedra increasing and the shape of octahedra less distorted.

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Hydrated Germanium (II): Irregular Structural and Dynamical Properties Revealed by a Quantum Mechanical Charge Field Molecular Dynamics Study

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Structural and dynamical properties of Ge (II) in aqueous solution have been investigated using the novel ab initio quantum mechanical charge field (QMCF) molecular dynamics (MD) formalism. The first and second hydration shells were treated by ab initio quantum mechanics at restricted Hartree-Fock (RHF) level using the cc-pVDZ-PP basis set for Ge (II) and Dunning double-zeta plus polarization basis sets for O and H. The radial distribution function (RDF) showed the maximum probability of the Ge-O bond length at 2.04 Å, accompanied by an extended first shell located at ~2.8 Å. A strongly distorted hydration structure with two trigonal pyramidal substructures within the first hydration shell is observed which demonstrates the lone-pair influence and provides a new basis for the interpretation of the catalytic and pharmacological properties of germanium coordination compounds.

Molecular dynamics simulations of ethanol-carbon dioxide mixtures along the liquid vapor coexistence curve

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Supercritical CO_2 and CO_2-expanded liquids (CXLs) are the alternate media for performing chemical reactions. Expanded liquids combine the beneficial properties of compressed CO_2 and of traditional solvents, leading to a new class of tunable solvents that are often the ideal type of solvents for a given application while simultaneously reducing the environmental burden. Supercritical CO_2-expanded ethanol is an advanced medium for high selective extraction possesses, formation of nanoparticles, nanofilms, and membranes because liquid ethanol dissolves large amounts of CO_2, expands greatly and consequently undergoes significant changes in virtually every physical property.

Molecular dynamics simulations have been performed for carbon dioxide - ethanol along the experimental liquid vapor coexistence curve in *NPT* ensemble at T=298K: two for the pure components and nine for the mixtures, containing 0.1-0.9 mole fraction x_2 of ethanol. The Zhang and Chen potential models have been used for CO_2 and ethanol, respectively.

The compositions and densities of the liquid phases of the binary system at equilibrium are critically compared with corresponding literature values. A satisfactory agreement was obtained between experimental and calculated phase compositions and saturated densities.

Structural properties of the mixture were investigated through the radial distribution functions (RDF), hydrogen bond network properties and the statistical geometry approach. H-bond analysis and dipole correlation functions show that the local geometry of the H-bonded ethanol molecules remains nearly unchanged with varying composition of the mixture. The ethanol molecules form the ramified chains in supercritical mixture even at 0.1 mole fraction of ethanol. The solute-solvent structure reorganization and preferential solvation of the mixture components are discussed in terms the local mole fractions of the *i* component molecule around a reference molecule of the *j* component x_{ij}^{loc}.

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Structure and Equilibrium of the Platinum - Thallium Cyanide Complexes in DMSO

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The metal-metal bond between platinum and thallium is well documented in aqueous solution.[1] There are four binuclear and one trinuclear species detected in solution which are formed from $Pt(CN)_4^{2-}$, Tl^{3+} and CN^- in reversible equilibrium reactions. There is a linear three atom center - four electron bond, Tl-Pt-C, involving the carbon atom of the axial cyanide ligand on the platinum site. In dimetylsulfoxide (DMSO) some new phenomena appear.[2] The main difference is that the metal-metal bond can be formed without coordination of the fifth (axial) cyanide to the Pt-atom.
The new compound in DMSO has been studied by multinuclear NMR, UV-VIS, EXAFS and DFT calculations.
EXAFS results show five DMSO ligands on the thallium site and only the four (equatorial) cyanide ligands on the platinum site, the axial coordination site of the Pt atom remains empty. Calculated structures by full geometry optimizations support this model. DFT indicates a strong metal-metal bond combining the $d(z^2)$ orbital of Pt and the 6s orbital of Tl. The absorption spectrum consists of several transitions including metal to metal and ligand to metal charge transfer bands according to Time-Dependent (TD) DFT calculations.

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THE INTRINSIC CONNECTIVITY OF METAL AQUAIONS AND POLYOXOANIONS IN AQUEOUS SOLUTIONS: AN AB INITIO MOLECULAR DYNAMICS STUDY.

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The Theory of Electrolytic Dissociation proposed by Arrhenius established a well defined separation between cations and anions. Their different sign and hydration properties have led to consider separately the formation of metal aquaions and polyoxoanions. The aim of this project is to show how aquaions are not only the most stable form of highly-charged metal cations, but also they can be considered in the origin of their corresponding polyoxo forms. This alternative reactant channel for the formation of polyoxoanions allows an unique view to stabilize ions of different sign in aqueous solutions.

The conversion from aquaions to polyoxoanions can be monitored in the case of S(VI) and Cr(VI) on the basis of ab initio molecular dynamics (AIMD) simulations. The results indicate the possibility of dealing with the formation of XO_4^{2-} (X being S or Cr) from their aquaions. The updating of the wave function of the system during the statistical trajectory allows an appropriate flexibility in the quantum mechanical description of the different species involved in the complex hydrolysis process which takes place. Moreover, the fundamental role of water molecules, which dissociate in order to reorganize the strong charge distribution, can be well modelled by AIMD simulations. Despite of being very time consuming, this methodology enables us to obtain a detailed microscopic picture of the chemistry of condensed finite temperature systems which can be compared to experimental data and used to investigate theories about reactivity and the origin of polyoxoanions.

Coarse-grained hydrated ions for lanthanides in water

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The study of hydration properties of ions in solution is usually performed by means of a cluster analysis on full-atom Molecular Dynamics (MD) trajectories, in which the solvation shell(s) are defined by simple geometric arguments or more elaborate dynamical considerations. This leads to a natural definition for the coordination numbers and hydration energies, but further thermodynamic or dynamical properties (osmotic coefficient, activities, conductivities, etc.) are difficult to obtain given the limitation on the length and time scales of these simulations. Thus, it is necessary to develop a simpler (i.e. continuum solvent) model, such as the Primitive Model (PM) in which the ions are assimilated to charged hard spheres. The problem is then reduced to finding a consistent correspondence between solvated ions in the molecular description and effective ions in the coarse-grained model.
We use an approach recently developed by us to provide a simple description of the thermodynamics and the structure for ion properties of two lanthanides (Nd+3 and Dy+3), which still takes into account the molecular aspects of the solvent, in terms of the well known Mean Spherical Approximation (MSA) and Binding MSA (BIMSA). The procedure is carried out in two steps. The first step consists in carrying out full-scale MD simulations to obtain the ion-ion correlation functions. For the second step Liquid Perturbation Theory (LPT) is used to compute the best simple soluble model possible (in terms of a mixed BIMSA/MSA model), which uniquely determines the solvated ion sizes. The final model is completely analytical and contains no free parameters.

APPARENT PROPERTIES OF SOLUTIONS FROM THE McMILLAN-MAYER (MM) PARTITION FUNCTION IN THE GRAND CANONICAL ENSEMBLE

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If we know how to calculate (or approximate) the MM partition function $\Xi_{MM}(T,V,\mu\sigma,\mu_s)$, of a solution (solute σ, solvent s), in the Grand Canonical Ensemble (GCE), then a theoretical scheme exists for obtaining the thermodynamic properties of the system. The MM theory gives directly the " apparent (molar) properties" which differ from the usual ones because the "natural variables " employed are those of the GCE. If X is an extensive property of the solution (pV, U, H, S, F, G, ...), then from Ξ_{MM} one can obtain $X\varphi^{MM}(T,V,\mu\sigma,\mu_s) = X(T,V,\mu\sigma,\mu_s) - X^*(T,V,\mu_s^*)$, with $\mu_s = \mu_s^*$ (pure solvent in osmotic equilibrium with the solution). These $X\varphi^{MM}$ are different from the usual ones defined as $X\varphi(T,p,n\sigma,n_s) = X(T,p,n\sigma,n_s) - X^*(T,p,n_s)$. In order to compare with the experiment , the changes of $X\varphi^{MM}$ with pressure must be included. In this work the general expressions are given and the simple case of an ideal solution in osmotic equilibrium with the solvent is explicitely considered as an example of the procedure to follow.

CHANGES OF SPATIAL STRUCTURE OF WATER IN SYSTEM "HYDROPHOBIC PARTICLE" - MOLECULES OF WATER.

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The computer simulation makes possible to find those structural characteristics which cannot be defined experimentally. It is determined by intermolecular interactions as well as the cavity formation. The new method of analysis of spatial relationships between molecules in the configurations of hydration shells is suggested. The properties of solutions are modeling using solute particles with hard sphere (the radius of HS: 1.6; 1.9 and 2.2Å) and Lennard-Jones (LJ) potentials, representing He, Ne, Ar and Xe. We also considered the LJ solute particles representing water molecule without the charge part of SPC potential. The calculations were carried out by Monte Carlo method in NVT ensemble for the systems containing 511 molecules of water and 1 solute particle at 300K and cell size, corresponding to density of water 1 g/cm^3. The processing of account results was carried out on samples of 100000 configurations.

The radial distribution functions g_{LJ-O}, g_{HS-O}, g_{OO}, g_{OH}, g_{HH} and spatial summary and partial functions $g(\alpha, \beta)$ have been obtained along with the partial functions corresponding to definite local densities of environment or coordination number (CN) of chosen water molecules in different spherical layers around dissolved particles (0.0 - 3.3A, 3.3 - 3.8A, 3.8 - 5.0A, 5.0 - 6.4A, 6.4 - 8.0A, 8.0 - 10.0A). The distributions of water molecules with various CN were obtained for each layer. They differ in comparison with pure water. It indicates that the state of water molecules changes in the first as well as in more distant layers. This effect is observed at the limited distance on which influence of the solute particle is tangible. The non-uniform structure of the first peaks of functions g_{LJ-O} and g_{HS-O} are shown. The spatial water angular correlations were established on the distances up to 8.0A. Tetrahedral configurations are dominating in this case. Solute particles are in the H-bond net cavities. These molecules of water in the first and the second spheres of the solute particle have different orientations. This molecules are surrounded more densely than in pure water due to additional LJ or HS neighbors. Tetrahedral neighborhood of such water molecules (CN = 3, 4) remains and even becomes more distinct.

As a result we have obtained an extensive graphical data characterizing the environment of different solute particle in details. It allows us to distinguish the specific effects of hydrophobic hydration for different non-polar particles.

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HYDROGEN BONDS IN PHOSPHORIC ACID - N,N-DIMETHYLFORMAMIDE SYSTEM: MOLECULAR DYNAMICS SIMULATIONS

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At present report the structural characteristics of H_3PO_4 DMF solutions were considered over the whole concentration range using molecular dynamics (MD) simulations. It was shown the most characteristic changes were observed for mixture H_3PO_4-DMF containing of 0.3 m.f. and 0.6 m.f. H_3PO_4. It was determined H-bond between H_3PO_4 and DMF molecules was significantly shorter then H-bond between H_3PO_4 molecules. The dependence of the average number of H-bonds (n_{HB}) was calculated over the whole concentration range. It was determined that hydrogen bonding complexes H_3PO_4-DMF were possible formed into infinite diluted solution H_3PO_4. The concentration dependence of n_{HB} has two characteristic minima at 0.3 m.f. and 0.6 m.f. of acid, which indicate the structural reorganization in solutions. Whereas n_{HB} between O(P)(H_3PO_4)...H(H_3PO_4) was monotone increased to 0.7 m.f. acid demonstrating enhancement of H_3PO_4 molecules structuredness in whole volume of mixture. Acid molecules were fully polymerized at high concentrations. This finding is confirmed by calculation of n_{HB} which was constant at 0.7 -1.0 m.f. H_3PO_4.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 08-03-00288)

Ab initio approach to determine specific interactions between teteraalkylphsphonium cations and amino acid anions in ionic liquids

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Ab initio calculations were performed using the Gaussian 03 software package to obtain the optimized structure, binding energy and infrared spectrum of ionic liquids comprised of tetramethylphosphonium cation and amino acid anions. The optimized structures of several ionic liquids in the gas phase were determined at the levels of Hartree-Fock (HF/6-31+G(d)) and density functional theory (B3LYP/6-31++G(d,p)). At higher level of calculations, MP2/6-31+G(d) and MP2/6-31++G(d,p), the binding energies between cation and anion were determined. In order to investigate the effect of alkyl chain length on the binding energy, alkyl group was varied from methyl to ethyl and propropyl in tetraalkylphophonium cation functional groups. This result reveals that there is a strong interaction of alkylphosphonium cation and amino acids. The results of the ab initio computations were in good agreement with data determined experimentally. However, a further rigorous research must be put into practice to confirm this study.

Protactinium(V) speciation in aqueous solution by ab initio quantum mechanics

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We interpret experimental Pa(V) aqueous speciation published data, mainly liquidliquid extractions. Our study is intended to take into account the influence of solvation on Pa(V), which appears to be fundamental in understanding Pa(V) specificity.
Mono-, di- and trications including Pa(V) in water are in limited number. We model all of them. B3LYP DFT is applied here to these cations surrounded by two explicit hydration layers.
PaO2+ similar to the other AnO2+ cations. It has strong apical bonds, resulting from the highly negative Oyl charge, which decreases along the An(V) series. This accounts for the instability of PaO2+ in water. PaO2+ diprotonates to give Pa(OH)23+ and can then dihydrolyse to give Pa(OH)4+ which is among be the most stable Pa(V) monocations.
PaOOH2+, the generally admitted Pa(V) dication, is confirmed to be the most stable for pH 1.4 ± 0.7.
PaO3+ is confirmed in sulfate solution, with a bond length close to 180 pm. Pa(OH)23+ has similar stability when modelled in water.
We test our two-shell model on fluorinated Pa(V). Fluoride coordination to Pa(V) is studied and compared with published EXAFS data: an excellent fit is obtained with the well established species PaF72-, whereas 6 and 8 coordination numbers are clearly less accurate. Since EXAFS are known to provide poorly accurate coordination numbers but very precise distances, the coupling of calculated and experimental distances appears to be very efficient in determining coordination numbers.

Non-ideality in single particle and pair dynamics of hydrogen bonded liquid mixtures

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We have investigated the dynamics of hydrogen bonded mixed liquids such as water-acetone, acetone-methanol and water-formic acid mixtures by means of molecular dynamics simulations. We have calculated diffusion and orientational dynamics of these solvent molecules and also the diffusion of ionic and neutral solutes in these mixtures for varying composition[1,2] . In particular we looked at the extent of nonideality in these single-particle dynamical properties as a function of composition of the mixtures. We have also calculated pair dynamical properties such as hydrogen bond and residence dynamics using the population correlation function approach [3,4]. Specifically, we have looked at the relaxation of water-water, water-acetone, acetone-methanol, methanol-methanol and water-formic acid hydrogen bonds and also the residence dynamics of the corresponding pairs in these mixtures for different composition. It is found that, unlike the single-particle properties like molecular diffusion and orienational relaxation, the pair dynamical properties do not show any maximum or minimum with variation of composition of the mixtures. While majority of the calculations are performed using classical potential models, some of the systems are also investigated by employing ab initio molecular dynamics[5] and the results of nonideal aspects are found to be qualitatively similar to those obtained using classical potentials.

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Electron and Li atom solvation in water and water - ammonia systems: Quantum chemical and *ab initio* molecular dynamics studies

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The solvation structures and energetics of an excess electron and lithium atom in water-ammonia systems in cluster and solvent phases are investigated by means of ab initio quantum chemical calculations and ab initio quantum simulations. We have mainly focused on the localization structure of the excess electron and solvent coordination to the metal ion and binding motifs of the free valence electron of the metal[1,2]. It is found that the hydrogen bonded structure of the anionic clusters are quite different from those of neutral clusters and presence of Li^+ counter ion in $Li(H_2O)_nNH_3$ affects the overall structures which are remarkably dissimilar from the pure anionic cluster structures. In case of pure anionic clusters like $[(H_2O)_nNH_3]^-$ both surface and interior-like binding states of the excess electron are found but in $Li(H_2O)_nNH_3$ the presence of the metal ion at the center of the cluster ensures that the ejected electron is solvated at a surface states. Results are also obtained for vertical detachment and vertical ionization energies of these systems and are compared with available experiments. The role of hydrogen bonds in the solvation of either an excess electron or a metal atom like Li in water and water-ammonia systems are also studied by means of finite temperature quantum simulations[3,4]. Vibrational spectral features are computed and one to one correlations are found between the time-averaged population of water molecules at different H-bonding sites with the calculated vibrational spectral features. The free electron-solvent correlations and various dynamical properties of the solvent molecules in the vicinity of the solvated electron and metal ion are also calculated in the present work.

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STRUCTURE-MAKING EFFECT OF TRIMETHYLACETATE-ION

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The trimethylacetate ion is widely used in coordination chemistry. Its properties as ligand appreciably differ from others carboxylates. Apparently, it is connected with distinction in solvation of this anion. However till now in the literature there are no data on its hydration. In the present work the kinetic aspect of hydration of trimethylacetate ion was investigated with use the microwave dielectric spectroscopy. The studies of high-frequency dielectric permittivity (ε') and losses (ε") of aqueous $(CH_3)_3CCOOK$ solutions are executed by the method of thin dielectric rod in a wave guide in the range of a maximum of the dipole losses of water at frequencies 13 - 25 GHz in temperature interval 288 - 308K. Low frequency specific conductivity of these solutions was studied also to calculation of ionic losses. The dispersion of complex dielectric permittivity is described by the Cole-Cole equations for all investigated temperatures and salt concentrations The values of dielectric relaxation time (τ) that characterize the changes of water molecule mobility in H-bond net were found with use of obtained experimental data on ε and ε. 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 $\Delta H_\varepsilon^{++}$ in $(CH_3)_3CCOOK$ solutions indicates on the structure-making influence of anion on the tetrahedral H-bond net of water. The comparison of these relaxation parameters was carried out in a number of others carboxylate solutions (potassium formate, acetate and propionate). The following order of τ and $\Delta H_\varepsilon^{++}$ changes in carboxylate solutions in comparison with pure water is observed: formate < water < acetate < propionate < trimethylacetate. As all these carboxylate ions have identical polar group and different nonpolar groups, the increase of τ and $\Delta H_\varepsilon^{++}$ values in solutions of carboxylates is determined by influence of nonpolar part. The presence of strong H-bonds in solutions between molecules of water and oxygen atoms of carboxyl group and practically absence of nonpolar part results in breaking of the tetrahedral H-bonds net of water by formate ion. The increase of the size of nonpolar part in the cases of other carboxylates compensates this effect and results in stabilization of water structure in propionate and trimethylacetate potassium solutions.

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Thermochromic VO_2 single crystal nanorods directly formed from a hydrothermal solution

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The synthesis of inorganic nanoscale materials with special morphologies has been of great interest in recent years. The binary oxide VO_2 is known to have different polymorphs, including VO_2 (R), VO_2(M), VO_2(B), VO_2(A) and VO_2(C), among which the VO_2(R) with the rutile crystal structure is the most stable one with a unique semiconductor-to-metal phase transition at around 340K. Upon the phase transition, the VO_2(R) exhibits an abrupt and reversible change in electronic, magnetic properties, and optically from highly transmitting to highly reflecting particularly in the infrared. The transition temperature can be tuned by element doping, making the VO_2(R) a promising material for "smart windows" as well as other electrical-optical switching devices.

In this study, single crystals of thermochromic VO2 were synthesized by reducing V_2O_5 with $H_2C_2O_4$ in a hydrothermal solution under a variety of temperature range. The VO_2(B) phase was formed at lower temperature, and it changed to VO_2(R) with increasing temperature. By adding a proper amount of H_2SO_4, the transformation of VO_2(B) to VO_2(R) was promoted, and monodispersed single crystal VO_2(R) nanorods were obtained directly from the hydrothermal solution for the first time. It was demonstrated that the H_2SO_4 was a very effective additive for the VO_2(R) formation and morphology control, believed to be closely related to the zeta-potential and dissolution-crystallization of the developed nanocrystals in the hydrothermal solution.

OSMOTIC AND ACTIVITY COEFFICIENT MODELING FOR TWO- AND THREE-BASIC AMINO ACID TERNARY SOLUTIONS

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The study of interparticle interactions in biologically active substance solutions is essential for the modeling of the processes in-vivo as well as for the understanding of salt effects in biosystems, especially for the molecular understanding of many ion-specific phenomena involving protein interactions in salt solutions. In this work we are concerned with the properties of glycine, aspartic acid, glutamic acid and their sodium salts. The chemical potential of these species has been studied with the help of vapor pressure osmometry and subsequent data treatment in following ternary systems: glycine + NaCl + H2O; glycine + KCl +H2O; glycine + NaNO3 + H2O; glycine +NaSCN + H2O; glycine +NaCOOCH3 + H2O; sodium L-glutamate + NaCl +H2O; sodium L-aspartate + NaCl + H2O; sodium L-glutamate + KCl + H2O; sodium L-aspartate + KCl + H2O at 310.15 K has been provided. The modeling for NaGlu + NaCl, NaGlu + KCl, NaAsp + NaCl, NaAsp + KCl systems has been provided with the use of the MSA model for ion mixtures with arbitrary radii. Electrostatic and hard sphere parts of the osmotic and activity coefficients have been analyzed and compared to the experimental data. More precise description of the concentration dependence of the osmotic coefficient is possible with the consideration of the degree of dissociation. From the consideration of the Gibbs-Duhem equation for the ternary systems of two electrolytes with common ion and of electrolyte-non-electrolyte mixtures, the activity coefficients of sodium salts with the background of glycine, sodium glutamate and sodium aspartate have been evaluated with the help of the activity coefficient values in the correspondent isopiestic binary solutions with the assumption that solution properties are additive and water activity and volume are constant in isopiestic solutions. The interaction parameters of binary and triple interactions have been derived from the fitting of the osmotic coefficients to the Pitzer equations for electrolyte-electrolyte and electrolyte-non-electrolyte solutions.

Hydrogen Bond Formation of Formamide and N-methylformamide using the Quantum Mechanical Charge Field Molecular Dynamics (QMCF/MD) approach.

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The formation of hydrogen bonds of formamide (CH_3NO) and N-methylformamide (C_2H_5NO) in aqueous solution was examined using QMCF/MD simulations. Their basic attributes like structure and solvation were compared with the results of the simulation. Hydrogen bond forming behaviour was investifgated in particular by means of distance plots, coordination number distributions (CNDs) and radial distribution functions (RDFs). Comparision of both molecules gave additional informations about the influence of methylation on the amide function.

Comparison of tetrahedron like oxo-anions in liquid water: an ab initio Quantum Mechanical Charge Field Molecular Dynamics study.

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Structure and dynamics of perchlorate, sulphate and phosphate have been investigated by means of Quantum Mechanical Charge Field Molecular Dynamics simulations. The obtained data are compared with recent experiments. The anion's librational and vibrational motions are presented and ligand exchange processes of water and spatial distributions of hydrogens are compared in detail.

Noble and Specific Lithium Ion Stabilization in TFSA Based Ionic Liquids

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Room temperature ionic liquids show favourable properties such as negligible vapour pressure, thus, practical implacability, a wide electrochemical potential window, and high chemical and thermal stability. Consequently, they are strongly expected as noble materials for the electrochemical devices of lithium ion secondary battery with highly safety. However, several problems have been pointed out in such an application. One of them is rather higher viscosity when the lithium ion concentration increasing, thus low ionic conductivity of the lithium ion in RTILs. On the other hand, if the solvation structure of the lithium ion in RTILs is revealed at a molecular level, the knowledge could lead us to the development of lithium ion secondary battery using RTILs of higher performance. Therefore, several literatures have been reported on the solvation structure of the lithium ion in RTILs by experimental [1] and theoretical [2] techniques.
Raman spectroscopy is one of the most powerful techniques for the isomerism of component ions of RTILs and solvation structures of metal ions in RTILs. We have so far investigated such issues by Raman spectroscopy and DFT calculations.[3]
In this contribution, thermodynamic quantities for the conformational isomerism of bis-(trifluoromethanesulfonyl) amide [TFSA] from trans isomer to cis one in $[C_4mIm][TFSA]$ ionic liquids ($[C_4mIm]$: 1-butyl-3-methylimidazolium) containing lithium ion were evaluated by means of Raman spectroscopy. It was quantitatively elucidated that the cis isomer of TFSA is more stabilized in the first solvation sphere of the lithium ion in ionic liquids, though the reverse is the case in neat and/or bulk ones. The finding was well supported by ab initio calculations for the isolated $[C_2mIm]\cdot[Li(TFSA)_2]$ model clusters in gas phase, i.e., the imidazolium cation evidently more stabilize the central lithium ion via the isomerization of TFSA solvated to the lithium ion, which is noble and specific lithium ion stabilization in TFSA based ionic liquids.

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Poster Session II

Posters 200-299

Anion Structure Effects on Solute-Solvent and Solvent-Solvent Interactions in Imidazolium Ionic Liquids

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While conventional organic solvents consist of single component, ionic liquids (ILs) are composed of an ion and its counter ion. In order to use ILs appropriately, it is important to consider the ion-counterion interaction and the ion-solute interaction, namely, solvation behaviour, in a microscopic environment. For instance, the equilibrium between free ions and ion-pairs in the imidazolium ILs has an influence on the reactivity of solutes surrounded with the ions.

We found that selecting a bulky camphorsulfonate, CS, anion for imidazolium cation results in decrease the anion-cation interaction and produces naked free ions more efficiently.[1] The free imidazolium cation facilitates the formation of the H-bonding between naked C_2-H of imidazolium ring and the H-bond acceptor such as a dienophile in a Diels-Alder reaction.[2]

In order to understand the influence of the anion structure on the ionic state furthermore, we systematically investigated using ILs with various sulfonate anions by using a specially designed ES mass spectrometry. It was shown that London dispersion force and π-π interaction as well as the anion size also affect the ion-pair formation and the interaction with the solute. In addition to the steric effect, we investigated the electrostatic interaction in the imidazolium ILs using negative charge delocalized anions with multiple electron-withdrawing cyano groups. Herein we report on the anion structure effects on the ionic state and the solvation behaviour from microscopic view in ILs media.

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Densities and Viscosities of Potassium Aluminum Sulfate in Water and Water + N, N-DMF Mixed Solvent at T = (298.15, 303.15, 308.15, and 313.15) K

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Measurements of densities and viscosities of potassium aluminum sulfate in water and water + (0 %, 5%, 10 %, 15 % and 20%) N,N-dimethylforamide have been made as function of molality at T = (298.15, 303.15, 308.15, and 313.15) K and at atmospheric pressure. Density data have been used to calculate the partial molar volumes of potassium aluminum sulfate. Viscosity data have been analysed by using Jones-Dole equation and B coefficients have been calculated. Partial molar volumes and B coefficients have been used to draw the conclusions regarding structure making or breaking behavior of potassium aluminum sulfate.

The coordination chemistry of lanthanoid(III) ions kindles the ionic radii of promethium(III)

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The coordination chemistry of the lanthanoid(III) ions follows a more regular pattern than any other series in the periodic table due to their identical outer shell electron configuration, $5s^2 5p^6$.[1] This makes the lanthanoids notoriously hard to chemically separate from each other, but ideal for comparative coordination chemistry studies.

We have studied the structures of the *N,N*-dimethylpropyleneurea (dmpu) solvated lanthanoid(III) ions in solution[2] and solid state[3,4] by EXAFS and single crystal X-ray diffraction. As a space-demanding solvent *at coordination*, dmpu often shows a coordination number lower than those found in hydrates and solvates of oxygen donor solvents without steric requirements beyond the size of the donor atom.[5] All lanthanoid(III) ions are six-coordinated in an octahedral fashion in the solid state, with a steadily decreasing Ln-O bond distance from lanthanum to lutetium. In solution they are seven-coordinated, except lutetium(III) which is six-coordinated in an octahedral configuration.

For a wider perspective, a comparative analysis has been performed on coordination numbers four to eight on all reported crystalline lanthanoid(III) structures solvated by monodentate oxygen donors.[6,7] Assuming an atomic radius of 1.34 Å for oxygen in dmpu, as in most *O*-donor ligands, the ionic radii of the lanthanoid(III) ions have been given refined values that in part differ from those listed by Shannon,[1] including interpolated values for the elusive promethium(III) ion.

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Volumetric and Acoustic Properties of Aqueous Solutions of Food Acids at (298.15 and 308.15) K

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Maleic acid, tartaric acid, and citric acid are food acids. Maleic acid is used as an acidulant in food and beverage industry. Its main use is in syrup, readytea, orange juice, sports beverage and other fortified syrup and food. Tartaric acid is widely used in food, medicine, and in pharmaceuticals. Citric acid is also used in food industry. Densities and ultrasonic velocities of aqueous solutions of citric acid, maleic acid, and tartaric acid have been measured at different temperatures and correlated with the molality of the solution. Density and ultrasonic velocity studies of aqueous solutions of citric acid have been reported earlier. From density and ultrasonic velocity data of aqueous solutions of maleic acid and tartaric acid, apparent molar volume, partial molar volume, apparent molar isentropic compressibility, partial molar isentropic compressibility have been calculated at 298.15 and 308.15 K. The results have been interpreted in terms of solute-solvent, solute-solute interactions and water structure making or breaking behavior of maleic acid and tartaric acid.

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Singular behavior of thermodynamic quantities of the binary mixtures near the critical points

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The investigation for mixture of supercritical fluids has been steadily increasing during the past decade. However, to date studies have been limited to low toxic materials such as water or the carbon dioxide or materials with low critical temperatures and/or pressures. The purpose of this study is to explore the origin of singular behavior of excess thermodynamic quantities of the binary mixtures near the critical points. In this work we calculated the excess thermodynamic quantities of model fluid mixtures using the PY integral equation, and compared the results with the experimental one. Model system is the two component fluid mixture interacting through the 12-6 Lennard-Jones potentials. The values of interaction parameters for component A are fixed at $\varepsilon_{AA}=1$ and $\sigma_{AA}=1$. The Lorentz-Berthelot rule is used for interaction parameters between unlike molecules. The values of interaction parameters for component B are determined so that the ratio of the critical temperature and pressure of two components for model fluids are corresponded to those of each component of the mixture of ethane - ethene system [1] and benzene - cyclohexane system [2]. The H^E were calculated in the wide range of temperatures and pressures. For the model system corresponding to ethane - ethane system, these values were negative in low temperature side and were positive in high temperature side, while they showed the S-shaped curves for composition in the middle temperature range. The most remarkable S-shaped behavior were observed between the two curves extended from the coexistence curve of gas and liquid to the supercritical region in p-T diagram. The S-shaped change can be ascribed to the phase transition like behavior. We made p/p_m-T/T_m diagram to compare this results with ethane - ethane system, where p_m and T_m are determined at the midpoint of two critical points. In this diagram, temperatures and pressures that S-shaped curves Obtained excellently agreed with them in each other systems. Also for the model system corresponding to benzene - cyclohexane system, the most remarkable S-shaped behavior can be ascribed to the phase transition like behavior. This indicates that the most important factor that determines the behavior of excess thermodynamic quantities near the critical point is the position of the state relative to critical point of each component.

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Solvent and solute dynamics in hydrophobic charged systems

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Non polar molecules usually cluster among themselves via hydrophobic-hydrophilic interaction to avoid direct contact with water molecules surrounding them (protein folding to micro-emulsion formation).The arrangement and dynamics of water molecules surrounding the hydrophobic solutes depend on solute-size [1].Moreover biological and organic molecules are often charged.The combined effect of hydrophobic and electrostatic forces on solvent dynamics remains unclear.To study such a system,we choose aqueous solution of Tetraalkylammonium salts (TAA).These salts are $NR_4^+X^-$ with $R^n = (CH_2)_{n-1}(CH_3)$ with X = Cl, Br or other halide ions,where the hydrophobicity increases with length of the carbon chain (increasing n).

Although our primary interest is in dynamics of the solute and solvent,prior understanding of the structure is essential.The TAA solutions were extensively studied under high concentration (about 1 molar) by neutron diffraction (ND) to reveal the water structure and apparently it is very similar to bulk water except for TBA (Tetrabutylammonium) [2].In ND we found also only a slight change in the D_2O peak position.No ion aggregation was seen in these highly concentrated solutions by Small Angle Neutron Scattering.

For exploring the dynamics in TAA aqueous solutions (using selective deuteration of either solute or solvent),we take advantage of quasi-elastic neutron scattering,more precisely Neutron Spin Echo (NSE).The dynamics of the system is contained in the energy transfer between sample and neutrons,which is measured in NSE through the change in neutron beam polarisation.Some dynamic data on TAA systems already exist (Time of Flight technique, NMR),suggesting a slowing down of water dynamics,as for simple alkali ions [3].Our NSE data for tetramethylammonium (TMA) solutions show relaxation time very similar to bulk water ($D=2.1*10^{-5}$ cm^2sec^{-1} and $D^{bulk}_{H2O}=2.3*10^{-5}$ cm^2sec^{-1}).For TBA,we find a value very near to that obtained by NMR [$(0.26 \pm 0.2)*10^{-5}$ cm^2sec^{-1}] [3].The Intermediate Scattering Function [I(Q,t)] from NSE is now to be compared with MD simulation as was done in our previous work [4], to properly decouple the signal from the ion and the solvent.

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Water distribution in concentrated sugar solutions: "water clusters" vs "3-dimensional network" models

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Concentrated sugars-water solutions are widely represented in both man-made materials (e.g., food and pharmaceutical products) and biological systems (e.g., dehydrated cells and organisms), and much attention is attracted to structure and dynamics of carbohydrate-water systems. In the present study, sucrose-water and sorbitol-water systems (water content 35 to 0 wt%) were studied by both thermally stimulated current (TSC) method and the differential scanning calorimetry. In addition, some molecular dynamics simulations, and both small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (XRD) experiments were performed. In both sugar-water systems, TSC detected several dielectric relaxation events, with a lower-temperature transition, T1, observed at 150 to 120 K. At low water contents, the T1 signal was either very weak (as in amorphous sucrose samples with 5 to 1% w/w water) or was not observed at all (amorphous sorbitol with 0% water). This observation suggests that the T1 relaxation is related to (rotational) mobility of water molecules. In sucrose-water system, temperature of the T1 event was independent of water concentration (30 to 1% water content), whereas in water-sorbitol system, the T1 temperature increased from 120K (35% water) to 150K (10% water). Interestingly, in pure water, dielectric relaxation was observed at ~140 K, i.e., in the same temperature range as the T1 event in sugar-water systems. This comparison implies that the rotational mobility of water molecules is essentially uncoupled from sugar molecules, as could be expected for the "water clusters" model. This interpretation is corroborated by the pairwise distribution function (PDF) analysis of the XRD data for the sorbitol-water sample. In addition, a detection of large-scale (>30 nm) inhomogeneities by SAXS for the same sorbitol-water solution provides an additional support to the "water clusters" model. Molecular dynamics simulations of sucrose-water system are, however, more consistent with a 3-d network ("spiderweb") of water molecules. The apparent difference in the conclusions based on different methods is being discussed.

Dielectric Spectroscopy of Propionate Hydration

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The carboxylate group, $-COO^-$, is an essential feature of many biologically relevant molecules, where its distribution on the molecular surface controls hydrophilicity and surface charge and where its presence is often decisive for solubility of these molecules in water and for their biological activity. Determining factor in the hydration of biomolecules is the relative balance of carboxylate-water versus water-water interactions in combination with the impact of hydrophobic moieties attached to $-COO^-$ on the structure of the surrounding water. Aiming at the separation of hydration effects associated with hydrophilic carboxylate from those induced by the hydrophobic alkyl tail, a systematic study of dielectric relaxation spectra of aqueous solutions of sodium propionate, H_5C_2-COONa, has been made up to the saturation limit, and over a wide range of frequencies ($0.2 \leq \nu$ / GHz ≤ 89) at 25°C. The spectra were best described by a superposition of three Debye processes, consisting of a relatively small process at ~1 GHz assigned to the ion pair relaxation (of amplitude S_{IP}), a relaxation at ~8 GHz, partly due to the reorientation of propionate anions (amplitude S_-), which bear a permanent dipole moment, μ_-, in addition to their charge, and to slow water hydrating the anions (amplitude S_w^{slow}), and a bulk-water relaxation at ~20 GHz (of amplitude S_w^{bulk}). By comparing the total amount of bound water, accessible from S_w^{bulk}, the known amount of H_2O molecules bound by the cation, and S_- estimated from μ_-, effective total hydration numbers and from amplitude of slow-water process, S_w^{slow}, hydrophobic hydration numbers for propionate were determined.

SOLUBILITY OF TRICYCLIC ACYCLOVIR DERIVATIVES IN CYCLODEXTRIN SOLUTIONS

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The purpose of this work is to find a way for enhancing the solubility of aqueous solutions of tricyclic analogs of acyclowir by hydroxypropyl-β-cyclodextrin.
Tricyclic analogs of acyclovir are obtained by modifications of guanine moiety in acyclovir by linking an etheno bridge to nitrogen atoms. Some substitutions at the TACV system proved to introduce desirable physicochemical properties with biological activity somewhat changed but still present.
In our previous study we have determined some thermodynamic and structural properties of this group of compounds including aqueous and octanol solubilities as well as octanol-water partition coefficients [1-3]. The determination of aqueous solubility revealed that the solubility of particular tricyclic analogs of acyclovir in water is various but always low (in the range from 10^{-3} - 10^{-5} mol kg^{-1}). They have good antivirial activity [4].
The subject of our present study are following tricyclic derivatives of acyclovir: 3,9-dihydro-3-[(2-hydroxyetoxy)methyl]-9-oxo-5H-imidazol[1,2-a]purine (TACV) and its substituted derivatives: 2-bromo-6-methyl(2-Br-6-Me-TACV); 6-tert-butyl (6-t-Bu-TACV); 6-phenyl(6-Ph-TACV); 6-(4-biphenyl)(6-Ph-Ph-TACV); 6-(2-naphtyl)([6-(2-napht)-TACV). The compounds were synthesized in the Institute of Bioorganic Chemistry of the Polish Academy of Sciences by Prof. dr B. Golankiewicz and co-workers.
The solubility of these compounds in aqueous buffered solutions of hydroxypropyl-β-cyclodextrin of different concentrations, using Higuchi and Connor method, at two physiological pH equal 5.5 and 7.0 and temperatures 25°C and 37°C, were determined. The results of investigation indicate that the aqueous solubility of tricyclic analogs of acyclowir, increase linearly with increase HP-β-CD concentration. The highest enhancement of solubility and equilibrium constant values were obtained for aromatic derivatives of tricyclic acyclovir. The enhancements of aqueous solubility of these species are in the range 3.3 to 7.7 at pH 5.5 and in the range 3.1 to 8.1 at pH 7 at 25°C. The increase of aqueous solubility of compounds without aromatic group is the same range 1.1 to 1.5 both at pH = 5.5 and pH = 7 and at 25°C and 37°C.
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Structural Properties of Diluted Aqueous RbBr Solution under Sub- and Supercritical Conditions

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The study of sub- and supercritical aqueous electrolyte solutions is a central topic in a variety of fields, since such systems play a crucial role in nature and in different industrial and environmental processes, such as oxidation of chemical and biochemical wastes, metal corrosion, selective synthesis and others. A fundamental understanding of the molecular level behavior of electrolyte solutions would be beneficial for realistic modeling of many physicochemical and biophysical phenomena including phase behavior, salt solubilities, etc.

The structural properties of a 0.5*m* RbBr(aq) solution under sub- (T=473 K, p=38.9 MPa, ρ=0.86 g/cm^3), near- (T=638 K, p=38.9 MPa, ρ=0.65 g/cm^3) and supercritical conditions (1. T=697 K, p=38.3 MPa, ρ=0.53 g/cm^3 and 2. T=697 K, p=63.3 MPa, ρ=0.64 g/cm^3), studied by the RISM integral equation method, are the subject of this report. The obtained data are compared to structural parameters under ambient conditions (T=298 K, p=0.1 MPa). Simultaneous increase of temperature and pressure leads to the destruction of the tetrahedral network of water and to the thermal dehydration of the ions. These structural changes are typical for hydrothermal solutions. In particular, the hydration numbers decrease by about 47% for Rb^+ and 33% for Br^- when going from T=298 to 697 K at 38.3 MPa (supercritical state 1). The dehydration is accompanied by a contraction of the Rb^+-O distance and an increase in Br^--O distance. Rising the pressure to 63.3 MPa at 697 K (supercritical state 2) increases hydration again by 16.6% for the cation and by 8% for the anion. The solution structure at sub- and supercritical conditions is characterized by the presence of an fraction of contact ion pairs which is increased by 13.6% relative to the value at ambient conditions (n_{CIP}=0.66). Solvent separated ion pairs are absent under all studied conditions.

This work was supported by the Russian Foundation for Basic Research (grant No. 09-03-97507-r_centre_a).

The Applicability of the ERAS Model to Excess Molar Volumes of Binary Mixtures of (Water + Organic Solvents) at Several Temperatures and p = 0.1 MPa

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The study of excess properties of liquid systems has been a qualitative and quantitative way to provide information about intermolecular interaction between components present in liquid mixtures. Moreover, the excess properties have been used to test and develop solution models and theories. As a continuation of our study involving volumetric properties, in the present work, experimental data of excess molar volume (V^E) of water + formamide, or + N,N-dimethylformamide or + dimethylsulfoxide or + N,N-dimethylacetamide or + 1,4-dioxane has been used to test the applicability of the Extended Real Association Solution Model (ERAS Model), as a function of composition, in the temperature range 288.15-303.15 K at p = 0.1 MPa. The ERAS-Model is a theoretical model based on statistical mechanical derivation. It combines the Kretscmer-Wieb Model of linear successive association with Florys equation state. The results obtained from the model are discussed in terms of intermolecular cross-associations with variation of temperature and organic solvent in the mixture.

Excess Molar Volumes of Binary Mixtures Containing Methyl *Tert*-butyl Ether (MTBE) and Alcohols at Several Temperatures and p = 0.1 MPa

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The study of excess properties of liquid systems has been a qualitative and quantitative way to provide information about intermolecular interaction between components present in liquid mixtures. As a continuation of our study involving volumetric properties, in the present work, densities of binary mixture of MTBE + methanol, or + ethanol, or + 1-propanol, or + 2-propanol have been used to determine the excess molar volumes, as a function of composition, in the temperature range 293.15-308.15 K at p = 0.1 MPa. Density measurements of liquid pure and mixtures were performed by means of vibrating-tube densimeter (Anton Paar, DMA 4500) which was calibrated with distilled water and air. Excess molar volumes are found to be negative, and become more negative as the temperature increases. The results obtained are discussed in terms of self-association in alcohol and cross-association between alcohol and ether molecules.

Density and Viscosity of (Biodiesel + Diesel) Mixtures at Several Temperatures

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Brazil is as an emergent potency in the production of biodiesel. Firstly, because Brazil has area and climatic conditions to create animals and cultivate different kind of the vegetables. Secondly, although ethanol is less reactive than methanol, Brazil is the biggest world producer of ethanol from sugar cane and the production of biodeisel using ethanol can become economically viable.

In this study, density and viscosity of biodiesel + diesel mixtures have been determined as a function of composition at several temperatures. Mixtures were performed by volume from B2 (indicates 2% of biodiesel with 98% diesel) to B100 (100% biodiesel). Biodiesel in this study was prepared through sodium ethoxide-catalyzed methanolysis from transesterification of the soybean oil. The optimum condition for reaction was: molar ratio oil-methanol 1:7, temperature of 60 ^{o}C, quantity catalyst of 0.8% wt and reaction time of 45 min, which enable a conversion of 94.64% by CG analysis. A series of test was performed to characterize the properties of the produced biodiesel. The results of density and viscosity are discussed.

Thermodynamics of the Ion - Lysozyme Association

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Addition of simple electrolyte can dramatically change the properties of protein solution. The phenomenon is most often explained by variation of the solvent mediated interactions between ions and proteins. However, the corresponding thermodynamic parameters, essential for understanding of ion - protein association at the molecular level, have not yet been determined. Presented work provides first complete thermodynamic study of ion - lysozyme association. The thermodynamic quantities are discussed in the light of Hofmeister series.

In the present study we employed isothermal titration calorimetry to measure the heat effects coming from salt - lysozyme interaction in aqueous buffer solutions (pH = 4.0, lysozyme mean net charge = +11). The calorimetric binding isotherms obtained for NaCl, NaBr, NaI, $NaNO_3$, NaSCN, KCl, $CaCl_2$, and $BaCl_2$ at different temperatures were described simultaneously by a model assuming independent binding sites for anions (counter-ions). Since the influence of cations (co-ions) on the measured heat effect appear to be weak, the presented global thermodynamic analysis allowed reasonable determination of the thermodynamic profile ($\Delta G°$, $\Delta H°$, $\Delta S°$, $\Delta C_P°$) for the anion - lysozyme association.

The resulting binding constants increase in order $Cl^- < Br^- < I^- < NO_3^- < SCN^-$.

This association is entropy driven accompanied by a small favorable enthalpy contribution and positive change in the heat capacity.

Dangerous Levels of Toxic Metals Found in the Ground Water in Tisayanvillai, South Tamil Nadu, India.

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One third of world's population depends on ground water for their livelihood, particularly for drinking. Contamination of drinking water by heavy metal ions could lead to dangerous physiological disorders. The concentrations of some inorganic components present in the drinking water in Tisayanvillai, a small town in South Tamil Nadu, India, have been investigated. While the quantities of calcium, magnesium, phosphate and sulphate present are well below the permissible standards, the amount of iron, lead and zinc present are alarmingly high and can cause adverse effects on human health. The survey of diseases recorded in the town also confirms this. The municipal authorities have been requested to take remedial measures.

DIELECTRIC RELAXATION AND CONDUCTIVITY OF POLYDIALLYLMETHYLAMMONIUM TRIFLUORACETATE AQUEOUS SOLUTIONS

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Solutions of polyelectrolytes find wide application in various fields of a science and techniques. In particular aqueous solutions of the polydiallylammonium salts have a high biological activity and are used in medicine. The information on hydration and transport properties of solutions is necessary for their optimum application.

In order to establish the features of molecular-kinetic hydration of polyelectrolyte, the microwave dielectric properties of aqueous solutions of polydiallylmethylammonium (poly(DAMA)) and diallylmethylammonium (DAMA) trifluoroacetates have been studied in temperatures interval 288-308K. Complex dielectric permittivity was measured by a method of thin dielectric rod in the wave-guide at frequencies 7.5, 10.0, 13, 16, 18.9, 22 and 25 GHz (in the region of maximum of dispersion of dielectric permittivity of water). The values of dielectric relaxation time τ were found. They characterize the changes of the water molecules mobility in the hydration shells of ions. The activation enthalpy $\Delta H_{\varepsilon}^{++}$, free energy $\Delta G_{\varepsilon}^{++}$ and entropy $\Delta S_{\varepsilon}^{++}$ of dielectric relaxation processes were calculated using the temperature dependences of τ. The growth values of τ and $\Delta H_{\varepsilon}^{++}$ was observed for poly(DAMA) and DAMA trifluoroacetates aqueous solutions. It indicates on the structure-making influence of ions on the tetrahedral hydrogen bond net of water. The concentration dependences of τ and $\Delta H_{\varepsilon}^{++}$ exhibit an opposite behaviour to that of the electrolyte solutions with typical hydrophilic hydration. Thus for the first time the hydrophobic hydration of polydiallylmethylammonium is established.

The conductivity of aqueous solutions of trifluoroacetic acid, poly(DAMA) and (DAMA) trifluoroacetates was investigated in a wide area of concentration, (including solutions with a high degree of dilution) for the establishment of features of ionic transport. Measurements are executed in temperature interval 288-308. It is revealed, that the equivalent conductivity of poly(DAMA) and (DAMA) trifluoroacetates solutions follows the linear dependence $\lambda=\lambda_{\infty} - Ac^{1/2}$ (where λ - equivalent conductivity, c molarity) up to 0,1 M in contrast to the cases of other polyelectrolytes and weak electrolytes. The limiting ionic mobility λ_{∞} for the trifluoroacetate, diallylmethylammonium and polydiallyl-methylammonium ions is found. It is shown, that process of charge transfer in the polydiallylmethylammonium aqueous solutions is realized, mainly, due to the migration of trifluoracetate -ion.

Acidic Ionic Liquids for Tetraphenylporphyrin Preparation

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Tetraphenylporphyrin, TPP, offers attractive features in a wide variety of model studies. Condensation of benzaldehyde with pyrrole in dichloromethane followed by oxidation generally provides TPP in a one-flask synthesis.[1] To keep using dichloromethane in favour of the efficiency, however, is likely to become more undesirable than ever particularly in green chemistry.

We study usage of ionic liquid, IL as a new medium for the porphyrin preparation. [bmim][NTf_2] shows similar yield (41%) to dichloromethane solvent as to porphyrin formation. However, the used IL is unlikely to be reused for the reaction due to the difficulty of removing the dissolved tarry by-products away from the IL. Then, we examined the use of acidic IL reported by Davis,[2] 3-butyl-1-(butyl-4-sulfonyl) imidazolium trifluoroethanesulfonate.

This acidic IL is immiscible with dichloromethane. A phase separated acidic IL to catalyze a reaction of pyrrole with benzaldehyde in dichloromethane, forming porphyrins in a comparable yield (43%) to Lindsey method. To minimize the amount of dichloromethane solvent, we examined the formation of the porphyrins at 10-fold higher reactant concentration, 145 mM, on the interface. In this case, it was possible to keep the comparatively high yield (27%) to ordinary method. Moreover, the IL phase is reusable at least 10 times without loss of catalytic activity.[3] Our results indicated the presence of the acidic IL phase through the interface facilitate the condensation in the dichloromethane phase, even at a high reactant concentration. In addition, this phase separated acidic IL is slightly dissolves in the dichloromethane.

We considered that the delicate dissolution of acidic ILs to the dichloromethane is important. Therefore, we investigated porphyrin preparation using various acidic ILs in order to evaluate the relationship between the lipophilicity and catalytic activity of ILs. In this presentation, the green porphyrin preparations utilizing IL would described in detail.

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Solvation structure of Li-ion in low-viscosity Ionic Liquid, 1-Ethyl-3-methylimidazolium Bis(fluorosulfonyl)amide studied by Raman spectroscopy

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Room temperature ionic liquids (RTILs) have been widely applied to green chemistry and electrochemical devices such as lithium-ion secondary batteries and capacitors, in recent year. RTILs are generally rather viscous compared with conventional molecular solvents. On applications, a RTIL involving bis(trifluoromethnesulfonyl)amide ($TFSA^-$) anion is generally used as a solvent due to its relatively lower viscosity and TFSA based RTILs containing metal ion, particularly Li^+ ion, has been investigated in view of electrochemical and physicochemical properties.[1] Recently, It was reported that RTIL involving FSA^- anion where CF3 groups of TFSA are substituted by F atoms shows a much lower viscosity than TFSA based RTIL.[2] Furthermore, it found that viscosity of EMI+TFSA- significantly increases with adding Li salt, on the other hand, that of EMI+FSA- is not significant. The extent of viscosity increase strongly depends on the solvation of Li+ ion in the RTIL.

To elucidate the solvation structure of Li^+ ion in EMI^+FSA^- ionic liquid, in this presentation, Raman spectra were measured for EMI^+FSA^- containing LiFSA salt. With increasing Li salt concentration, Raman band at around 730 cm^{-1} weakens and then a higher shifted band intensifies. The former band is assigned to the FSA^- in the bulk and the latter to the FSA^- bound to Li^+ ion. By analysing the Li concentration dependence on Raman spectra observed, it revealed that Li^+ ion is solvated with three FSA^- ions in EMI^+FSA^- ionic liquid. Here, it has been established that solvation number of $TFSA^-$ around Li^+ ion is two in EMI^+TFSA^- ionic liquid and the solvated TFSA binds to Li^+ ion through O atom as a bi-dentate ligand.[3] The solvation number estimated in the EMI^+FSA^- system is largely different from that in EMI^+TFSA^- system, although molecular structure is almost the same between FSA and TFSA. To elucidate the solvation structure of Li-FSA system in detail, temperature dependence on Raman spectroscopy is studying now.

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Understanding of CO_2 Dissolution Effects on 1-Alkyl-3-methylimidazolium Salts by Several Experimental Techniques

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Ionic liquids (ILs) show remarkable solubility of acidic gases such as carbon dioxide, SO_x, and NO_x. The *pVT* behaviours in CO_2-IL systems have been reported for typical imidazolium salts. Several researchers successfully provided meaningful insights into molecular interactions in such systems; however, most of them were studied only by computer simulations. Here, we investigate solute-solvent interactions in 1-alkyl-3-methylimidazolium salts $[C_nMIM]X$ with $X = PF_6^-$, BF_4^-, and $[(CF_3SO_2)_2N]^-$ mixed with CO_2 at high pressures by several experimental techniques, conductometry, chronoamperometry, NMR relaxatiometory, and X-ray diffractometry.

The effect of CO_2 on transport phenomena in $[C_nMIM]X$ is very remarkable. The electrical conductivity increased with increasing CO_2 pressure.[1] The diffusion coefficient of ferrocene in ILs also increased with increasing CO_2 pressure. These results show that CO_2 dissolution breaks down inter-ionic interactions between the cation and anion species, leading to more mobile situation in ILs. Moreover, structural studies suggest that CO_2 is favourably solvated to the fluoro-anions in ILs.[2] In the present work, we would comprehensively understand the effects of CO_2 dissolution in $[C_nMIM]X$-CO_2 systems.

This study was partially supported by Industrial Technology Research Grant Program in 2007 from New Energy and Idustrial Technology Development Orgazization (NEDO) of Japan.

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Hydrogen bonding in the crystal structures of new imidazolium triflimide protic ionic liquids (PILs)

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The synthesis and crystal structures of 1,3-diamino-2-methylimidazolium bis(trifluoromethylsulfonyl)imide (1), 1,3-dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide (2) and 1-(2-(diethylammonio)ethyl)-3-methylimidazolium bis(bis(trifluoro-methylsulfonyl)imide) (4) are reported. The salts 1, 2 and 4 have melting points below 100 °C, the intermediate 1-(2-(diethylamino)ethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (3) is liquid at room temperature. Ironically, crystallography is the most powerful tool for the elucidation of interactions in ionic liquids or low-melting salts. Three markedly different hydrogen bonding architectures were observed in the crystal structures of the three new protic imidazolium triflimides. The ions in 1 build a network of N-H...O hydrogen bonds, in 2 they are linked to chains by O-H...N and bifurcated O-H...O hydrogen bonds, whereas in 4 they form pairs by N-H...O contacts. The triflimide anions adopt transoid conformations.
In summary, the "non-coordinating" triflimide anion displays interactions with protic cations via oxygen and nitrogen atoms.

The Solution Enthalpies of Phosphoric Acid in Water N,N-Dimethylformamide Mixtures

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Earlier viscosities, refractive indexes, and conductivities of phosphoric acid in water N,N-dimethylformamide mixtures over the whole concentration range of components have been studied [1]. Conductivity data showed that ionic dissociation of phosphoric acid decreases with DMF content and increases in mixed solvent H_2O + DMF. At DMF concentrations in mixed solvent H_2O DMF more than 0.3 m.f., ionic dissociation of H_3PO_4 becomes small. The dependence of some properties (viscosity, refraction index) of H_3PO_4 solutions in mixed solvent H_2O - DMF (when $x_{DMF} > 0.3$ m.f.) as acid concentrations has a maximum with position at about 0.6 acid mole fraction independently of H_2O + DMF composition. This is evidently caused by the molecular association processes in the acid itself.

Now the molar enthalpies of solution of phosphoric acid at various molarities in water dimethylformamide mixtures were measured by isoperibol calorimeter at 298.15 K. Because there are several processes in the studied solution, namely, ionic dissociation, molecular association, and destruction/formation of H-bonds, the values of standard solution enthalpies of H_3PO_4 dissolution $\Delta_{sol}H^o$ were calculated by polynomial fitting. The dependence of $\Delta_{sol}H^o$ from composition mixture solvent passes through a maximum at the small amount of water mixture.

We would like to thank the Russian Foundation of Basic Research (project No. 08-03-00288) for the financial support of this work.

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SOLUBILITY OF FULLERENE C_{60} IN MIXED ORGANIC SOLVENTS

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Fullerenes have attracted considerable attention due to the fact that using polyhedral carbonic clusters and their derivatives in high-tech industries holds great promise. Numerous aspects of application of fullerenes are connected with their state in the solvent medium. Fullerenes are known to form crystallosolvates (molecular complexes of Van-der-Waals nature) with many organic solvents. Formation and disruption of such complexes play a very important part in dissolution of fullerenes and understanding the fullerene-solvent interaction. However, studies of mixed solvation complexes formed by two or more molecules of various organic solvents have hardly been reported, though the probability of such complexes being formed is rather high.
Data on solubility of C_{60} in mixed solvents: tetrachloromethane (CCl_4) toluene, CCl_4 *o*-dichlorobenzene ($C_6H_4Cl_2$), tetralin ($C_{10}H_{12}$) CCl_4, $C_{10}H_{12}$ $C_6H_4Cl_2$ and CCl_4 $C_6H_4Cl_2$ were obtained by us in range of they concentration and in temperature interval 298.15 - 338.15 K. The original experimental setup has been utilized for these measurements. 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 of 5%. It should be noted that in mixture $C_{10}H_{12}$ $C_6H_4Cl_2$ solubility of C_{60} is much high, than in pure components. Maximum solubility was observed in binary solvent with X $C_{10}H_{12}$ = 0.3 - 0.5 at lower temperatures. Enthalpies and temperatures of incongruent melting point of obtained crystallosolvates have been determined by differential scanning calorimetry (DSC 204 F1 Phoenix, NETZSCH). A method was tested of determining stoichiometric composition of fullerene crystallosolvates using FT-IR (Vertex 80, Bruker).
Were shown that solvates C_{60} to form with both components with mixed solvents. The stoihiometric composition was determined. It was found that the entropy factor is predominant in the change Gibbs energy solvation of C_{60} in individual solvents and their mixes. The main contribution to salvation entropy is made by the effect cavity formation.
This work has been done under the financial support of Russian Foundation for Basic Research (RFBR), project 08-03-00513

PHENOL AND BENZOIC ACID PREFERENTIAL S... IN BINARY AQUEOUS-ORGANIC MIXTUR...

P-222

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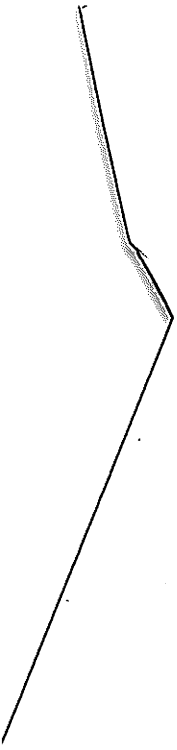
A possibility of solute preferential solvation by one of the mixture compone... in non-ideal binary mixtures. This preferential solvation may present the ... the sorption process on polymer.

This work provides a study of phenol and benzoic acid dissolution in ... aqueous-organic mixtures water-dimethylsulfoxide (DMSO) and water-acet... (AN) and their sorption on cellulose. Phenol and benzoic acid solubility ... determined at 298 K using isothermal saturation method; heats of phenol and benz... acid dissolution. The sorption isotherms of DMSO, AN and water on cellulose fro... binary solutions water-DMSO and water-AN were obtained. The immersion heats of cellulose in the water-DMSO and water-AN systems were measured.

Based on analysis of literature and experimental data an assumption is made, that the solvation features of both phenol and benzoic acid as well as sorption on cellulose are due to the features of intermolecular interactions in binary water-DMSO and water-AN mixtures. In contrast to benzoic acid the thermodynamic characteristics of phenol dissolution as well as sorption character on cellulose change drastic at concentrations corresponding to change of character of cluster formation in water-DMSO and water-AN mixtures. Differences in phenol and benzoic acid solvation as well as sorption on cellulose can be explained by different interaction mechanisms of solutes with existing in binary aqueous-organic mixtures clusters.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 07-03-00300-a)



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PHENOL AND BENZOIC ACID PREFERENTIAL SOLVATION IN BINARY AQUEOUS-ORGANIC MIXTURES

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A possibility of solute preferential solvation by one of the mixture components appears in non-ideal binary mixtures. This preferential solvation may present the key-item in the sorption process on polymer.

This work provides a study of phenol and benzoic acid dissolution in binary aqueous-organic mixtures water-dimethylsulfoxide (DMSO) and water-acetonitrile (AN) and their sorption on cellulose. Phenol and benzoic acid solubility was determined at 298 K using isothermal saturation method; heats of phenol and benzoic acid dissolution. The sorption isotherms of DMSO, AN and water on cellulose from binary solutions water-DMSO and water-AN were obtained. The immersion heats of cellulose in the water-DMSO and water-AN systems were measured.

Based on analysis of literature and experimental data an assumption is made, that the solvation features of both phenol and benzoic acid as well as sorption on cellulose are due to the features of intermolecular interactions in binary water-DMSO and water-AN mixtures. In contrast to benzoic acid the thermodynamic characteristics of phenol dissolution as well as sorption character on cellulose change drastic at concentrations corresponding to change of character of cluster formation in water-DMSO and water-AN mixtures. Differences in phenol and benzoic acid solvation as well as sorption on cellulose can be explained by different interaction mechanisms of solutes with existing in binary aqueous-organic mixtures clusters.

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A ground-state QM/MM model of a photoacid to study excited-state proton transfer reactions

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Photoacids are weak acids in the ground state, but become strong acids in the excited state. They are widely used in experimental investigations of proton-transfer reactions, as the excitation of the acid by a UV pulse allows to establish a time t=0 for kinetic measurements. 8-hydroxy-1,3,6-trisulfonated pyrine (HPTS) is a photoacid commonly used in such experiments. Here, we use 2,4,6-Tricyanophenol (TCN) in the ground state as a model for HPTS in the excited state. The QM/MM approach consists in replacing the cyano-groups with a point-dipole moment, which allows to "tune" the acidity of TCN such as to reproduce the acid properties of excited-state HPTS. The solvent is treated completely at the QM level in order to allow the transfer of protons. A brief introduction to the model is presented, as well as results of a 250 ps molecular dynamics simulation (DFT). The results are encouraging and suggest that our model is able to reprodue the acid properties of HPTS in the excited state.

The Iodide Anion in Liquid Water: an ab initio Quantum Mechanical Charge Field Molecular Dynamics Study

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The new ab initio QMCF MD methodology was applied to iodide in aqueous solution. The structure breaking ability of the anion results clearly from the evaluation of the trajectory and allows a quantification of the dynamics of the iodide hydration.
The structure-breaking behaviour of iodide is clearly visible from all detailed data obtained by the simulation. Hydrogen bonds between water and the anion are extremely short-lived (0.26 ps) and thus more rapidly formed and broken than between solvent molecules.

Vapor-Liquid Equilibrium Properties of Sodium n-Pentyl Sulfonate in Water, in Aqueous Solutions of Poly(ethylene glycol) and in Aqueous Solutions of Poly(vinyl pyrrolidone)

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It has been generally recognized that studies of thermodynamic and transport properties of surfactants are important to understand their behavior in solutions [1]. The interaction between polymers and surfactant in aqueous solutions has also become a very interesting topic for widespread application such areas as oil recovery, colloid stability, surface modification, wetting, and the physiological transport and metabolism of lipids and their interaction with proteins as well as theoretical studies and has been investigated for several decades and extensively documented [2]. Surfactants may bind cooperatively to nonionic water-soluble polymers to form micelle-polymer complexes [3], and these interactions are largely confined to anionic surfactants. Regarding to the thermodynamics of binary aqueous solutions of anionic surfactant and ternary aqueous solutions of polymer-anionic surfactant, sodium alkyl sulfates [CH_3–$(CH_2)_{n-1}$–SO_4Na], especially sodium dodecyl sulfate ($C_{12}SO_4Na$), have been extensively studied. Sodium alkyl sulfonates [CH_3–$(CH_2)_{n-1}$–SO_3Na] are one of the most important class of anionic surfactants that are structurally closely related to sodium alkyl sulfates. Although, sodium alkyl sulfonates can form micelles in aqueous solution and also may interact with water soluble polymers such as poly(ethylene glycol) (PEG) or poly(vinyl pyrrolidone) (PVP) in aqueous solution, however, there is a very limited information about thermodynamics properties of aqueous solutions of sodium alkyl sulfonates. In this study, the vapor-liquid equilibria properties of sodium n-pentyl sulfonate (C_5SO_3Na) in pure water, in aqueous PEG solutions and in aqueous or PVP solutions were determined below and above the micellar composition range. Vapor-liquid equilibrium data such as water activity, vapor pressure, osmotic coefficient, activity coefficient and Gibbs free energies were obtained through isopiestic method. The concentration dependence of the all investigated thermodynamic properties exhibit a change in slope at the concentration in which micelles are formed. It was found that, the vapor pressure depression for ternary aqueous C_5SO_3Na + PEG and C_5SO_3Na + PVP systems is more than the sum of those for the corresponding binary solutions.

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Structure and Dynamics of Li^+ in Aqueous Solution

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The new ab initio QMCF molecular dynamics methodology was employed to obtain details of structure and dynamics of the Li^+ ion in aqueous solution. Radial and angular distribution functions and coordination number distributions were extracted to characterise the microspecies formed in water, and exchange dynamics were determined via mean ligand residence times. The structure-forming ability of the ion extends up to higher solution temperatures.

Although Li(I) in water is structure building, it is subject to many ligand exchanges on the picosecond scale, which would enable fast binding to biomolecules. A change of temperature to biological values (~ 37℃) will not affect Li(I) ion's structure making ability, but slightly increase exchange rates.

QMCF-MD Simulation of Co^{2+} and Ni^{2+} in Water

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This work describes ab initio QMCF MD simulations of hydrated Co^{2+} and Ni^{2+} ions. Structural and dynamical features were extracted from 10 ps trajectories.
Structural differences between the d^7 ion Co(II) and the d^8 ion Ni(II) in water are very minor, differences are observed, however, in the hydration dynamics of the second shell, which seems less volatile for Ni(II) than for Co(II). in accordance with the first shell exchange rates (which are far too slow to be observed in our simulation).

Hg(II) Hydration. An ab initio Quantum Mechanical Charge Field Molecular Dynamics Study

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The new ab initio QMCF molecular dynamics methodology was employed to obtain details of structure and dynamics of the Hg(II) ion in aqueous solution. Radial and angular distribution functions and coordination number distributions were extracted to characterise the microspecies formed in water, and exchange dynamics were determined via mean ligand residence times.
The QMCF simulation has produced the most accurate structural and dynamical details for hydrated Hg(II), whose coordination number is 7 in average in full agreement with EXAFS data. Numerous exchange processes within the picosecond scale make the hydration structure highly flexible and because of both associative and dissociative mechanisms asymmetric.

Structure and Dynamics of Hydrated Ag(I) - Ab Initio Quantum Mechanical/Molecular Mechanical Simulation

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To describe the structure and dynamics of Ag(I) in water a quantum-mechanical charge field molecular dynamics (QMCF MD) simulation was performed. QMCF MD simulates the first and second hydration shell with quantum-mechanical forces and the outer region with molecular mechanical potentials. To analyse the simulation Radial Distribution Functions, Mean Residence Times and Coordination Number-Distributions were evaluated. The results were compared to XRD and EXAFS-experiments and to other simulations.

The hydration structure of Ag(I) in water is irregular. The quantum effects seem esssential to describe the structure and dynamics of solvated Ag(I), and a large QM zone including the second shell is required to achieve the required simulation accuracy.

Study of a Cd^{2+} ion in aqueous solution by an ab initio QMCF MD simulation

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In this study the structural and dynamical properties of Cd^{2+} in aqueous solution are analysed. The system of one thousand molecules of water and one cadmium ion is simulated by the quantum chemical charge field (QMCF) molecular dynamics (MD) method at Hartree-Fock level. The results are illustrated by radial distribution functions (RDF), angular distribution functions (ADF) and coordination number distribution (CND).

The hydration shell of Cd(II) in water is much more stable than that of Hg(II), but the simulation indicates a not too long mean residence time of first shell ligands. This points to a relatively easy binding to other ligands in exchange for water. Structural data supplied by the QMCF simulation agree very well with XD.