ICSI Yamaguchi

27th
International Conference on Solution Chemistry
(27ICSC)

August 26-31, 2001
Vaals, Netherlands

Sponsored by IUPAC
and
Deutsche Bunsen-Gesellschaft
für Physikalische Chemie

Vaals in the
heart of Europe

Contents:

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Acknowledgement of Financial Support:

Deutsche Forschungsgemeinschaft (DFG)

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Welcome Message

The Rheinisch-Westfälische Technische Hochschule (RWTH) has the privilege to organize the 27. International Conference on Solution Chemistry (27ICSC). RWTH is the largest Technical University in Germany and a leading one in Europe. Situated in Aachen at the boarders of Germany, Belgium and Netherlands it has an international flair and attracts among its 30,000 students many from abroad. Founded in 1870 to promote engineering, mining and metallurgy in the industrial area of the western provinces of Prussia, the basic sciences including chemistry were established right at the beginning. Landolt who is internationally famous held the first chair in chemistry.

The city of Aachen has a history dating back to the Romans, and it was the capital under king Charles the Great (768-814) when France and Germany were under his common rule. The famous cathedral, the octagon, was built for his court and contains his tomb. For nearly 600 years, from 936 to 1531, Aachen with its cathedral was the coronation place for the German kings.

The site of the 27ICSC is the neighboring Dutch town Vaals which also dates back to the 11. century. As the name of the country, The Netherlands, suggests one does not expect hills or even mountains. Indeed the highest point of The Netherlands is near Vaals measuring 322 m. We gather in Kasteel Vaalsbroek a mansion first mentioned in 1420 and essentially shaped by the rich textile merchant von Clermont in the years 1761 to 1786. Today it is a conference center and a luxurious hotel is associated with it.

The local organizers, professors of physical chemistry of RWTH Aachen, welcome you to the 27ICSC and hope that the relaxing atmosphere of Kasteel Vaalsbroek will help to make our conference scientifically successful and socially enjoyable.

Aachen and Vaals, August 2001

Andreas Dölle
Joachim Richter
Wolfgang Stahl
Manfred Zeidler

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Program

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	So 26	Mo 27		Di 28		Mi 29		Do 30		Fr 31	
8.00–9.00		Breakfast									
9.00–9.20				Angell		Fries		Madden		Klein	
9.20–9.40		Opening									
9.40–10.00		Lynden-Bell									
10.00–10.20				Kolker	Alves-Marques	Cummings		Zakharov	Sismanoglu	Snook	
10.20–10.40				Lyashchenko	Buchner			Lileev	Spangberg		
10.40–11.20		Coffeebreak									
11.20–11.40		Lomba		Rossky		Weingaertner		Oye		Ackerson	
11.40–12.00											
12.00–12.20		Bako	Atik	Majer	Chialvo			Nezbeda	Tominaga	Turq	Belloni
12.20–12.40		Puhovski	Baev	Marcus	David	Watson	Kirillov	Ospanova	Turq	Okada	Kunz
12.40–13.00		Rothschild	Bagno	Mizuno	Dibrov	Yamaguchi	Laenen	Pavel	Umebayashi	Volkovich	Martinet
13.00–14.20		Lunch									
14.20–14.40		Ohtaki		Grolier		Excursion		Bessada			
14.40–15.00									chair		
15.00–15.20		Durov	Alves-Marques	Nomura	Gomez-Estevez			Persson	Wakisaka		
15.20–15.40		Fedorov	Apelblat	Ostapchuk	Hefter			Probst	Versmold	Kunz	
15.40–16.00		Francesconi	Balankina	Takamuku	Hermansson			Radnai			
16.00–16.20	Registration	Kiselev	Boitsov	Waghorne	Ishiguro			Safonova			
16.20–17.00		Coffeebreak						Coffeebreak			
17.00–19.00		Posters: Barcza Baev Branca Durov Francesconi Kurtoglu Magazu Snook		Posters: Branca Francesconi Fumino Gaspar Hefter Imano Kanno Magazu Viana				Posters: Baev Kagan Nilsson Pura Salabat Tomsic Viana Yonehama			
19.00–20.30	Dinner										
20.30–22.30	Welcome Party	Posters: Ahn-Ercan Arh Cerar D'Angelo Fadeeva Rudan-Tasic Tamiya Yoshida		Concert		Posters: Baev Branca Kajiwara Kameda Keceli Kirillov Magazu Maljkovic Nesterenko		Posters: Abbas Branca Bester-Rogac Gunnarsson Magazu Turq Volkovich Yamaguchi			

Molecular Liquids

Invited Lectures:

E. Lomba et al.: Molecular fluids and solutions adsorbed in porous media. A new challenge for integral equation theory.

R.M. Lynden-Bell et al.: Thermodynamics of solvation of small hydrophobic and hydrophilic solutes in room temperature and supercritical water.

H. Ohtaki: Are hydrogen bonds strengthened or broken by elevating temperature and pressure?

Oral Contributions:

I. Bako: Ab-initio molecular dynamics simulation of liquid formic acid.

Y.P. Puhovski et al.: MD simulation of liquid formamide and N,N-dimethylformamide with a new ab-initio potential.

W.G. Rothschild: MD simulations of liquid chloroform at 298 and 229 K using a fractional charge model. Comparison with Raman and neutron scattering results.

Poster Contributions:

L. Barcza et al.: Acetic anhydride as solvent or additive in analytical chemistry.

I.K. Snook et al.: Characterization of the structural and dynamical behavior of curved interfaces of simple fluids in free-film, slit-like and cylindrical pore systems by molecular simulation.

Non-electrolyte Solutions

Invited Lectures:

C.A. Angell: Molecular liquids and their solutions interpreted in the "landscape" paradigm.

P.J. Rossky: Water at interfaces.

J.P. Grolier: Experimental approaches in non-electrolyte solutions.

Oral Contributions:

Z. Atik et al.: Phase equilibria of binary mixtures of halogenated hydrocarbons.

A.K. Baev: Thermodynamic and specific intermolecular interactions in solutions of non-electrolytes with pentacoordinated carbon atom.

A. Bagno et al.: Probing the solvation shell of organic molecules by intermolecular 1H NOESY.

V.A. Durov: Modeling of supramolecular ordering in mixtures. Structure, dynamics and properties.

V.A. Fedorov: The complexation in mixed water-organic solvents.

A.Z. Francesconi et al.: Modeling of excess molar volume of acetonitrile with amine using the Prigogine-Flory-Patterson theory.

M. Kiselev et al.: Study of hydrogen bonds network in water-alcohol mixtures at ambient, sub- and supercritical condition.

A.M. Kolker et al.: Water-organic mixtures at normal and high pressures: Thermodynamic properties and structure.

A.K. Lyashchenko et al.: Dielectric relaxation and structural-kinetic changes in aqueous non-electrolyte solutions.

V. Majer et al.: Towards a prediction scheme for hydration properties of aqueous hydrocarbons up to the critical region of water.

Y. Marcus: Preferential solvation in completely miscible aqueous co-solvent binary mixtures at 298.15 K.

K. Mizuno: Effects of polar groups on hydrophobic hydration probed by 1H and 13C NMR chemical shifts and frequencies of C-H stretching vibration bands.

H. Nomura et al.: Utrasonically induced birefringence of polymer solutions.

Y.L. Ostapchuk et al.: Dynamics of equilibrium establishment of the inhomogeneous solution methanol-hexane near the separation critical temperature.

T. Takamuku et al.: Large-angle X-ray scattering, small-angle neutron scattering and NMR relaxation studies on cycloether-water binary mixtures.

W.E. Waghorne et al.: Enthalpy of transfer of -CH2- between water and organic solvents or mixed aqueous organic solvent systems.

I.D. Watson: The thermodynamic behavior of solutions. Is a generalized approach feasible?

T. Yamaguchi et al.: Structure of ethanol-water binary mixtures by neutron diffraction, empirical potential structure refinement and spherical harmonic expansion analysis.

A.G. Zakharov et al.: An application of mass spectrometry to study the water properties on the cellulose material interface.

Poster Contributions:

A.K. Baev et al.: Solvates and specific interaction in solutions of methyl compounds subgroup of aluminium.

C. Branca et al.: Thermo-physical properties of disaccharide aqueous solutions.

C. Branca et al.: Vibrational dynamics in hydrogen bonded system aqueous solutions.

C. Branca et al.: Analysis of structural changes of water in trehalose aqueous solutions.

C. Branca et al.: Raman scattering and acoustic measurement on polymeric aqueous solutions.

V.A. Durov et al.: Models of alcohol mixtures. Supramolecular ordering, thermodynamic and electrooptical properties.

A.Z. Francesconi et al.: Volumetric properties of binary mixtures of acetonitrile and amines at different temperatures and atmospheric pressure.

A.Z. Francesconi et al.: Correlation and measurement of molar excess Gibbs free energy at 323 K and molar excess enthalpy at 298 K and 343 K for water /1,2-propanediol, water/1,3-propanediol and water/1,4-butanediol.

H. Kanno et al.: Supercooling of aqueous solutions of alcohols and sugars.

A.E. Kurtoglu et al.: Adsorption of mitoxantrone on glass powder.

S. Magazu et al.: Analysis of the L-ascorbic acid / water interaction by neutron scattering.

S. Magazu et al.: Neutron scattering study on fragile glass-forming aqueous solutions.

S. Magazu et al.: Study on fragility of vitamin C / water system across glass transition.

S. Magazu et al.: Study of hydrogen bonded systems coordination by viscosity and ultrasonic velocity measurements.

D. Rudan-Tarsic et al.: Thermodynamics of aqueous solutions of some lower polyethylene glycols.

Y. Tamiya et al.: The comparison of molecular dynamics simulations with the picture of hydration of non-electrolytes obtained from IR and NMR measurements.

K. Yoshida et al.: Microscopic structure of clusters formed in hexafluoroisopropanol – water mixtures.

Electrolyte Solutions

Invited Lectures:

P.H. Fries et al.: Theories of structural and dynamical properties of ions in discrete solvents. Application to magnetic resonance imaging.

P.T. Cummings et al.: Molecular modeling and simulation of supercritical water and aqueous solutions.

H. Weingaertner: Corresponding states in electrolyte solutions.

Oral Contributions:

M. Alves Marques et al.: Local order in concentrated aqueous solutions of salts containing ions of different valencies. X-ray diffraction investigations.

M. Alves Marques et al.: Positional correlations in concentrated aqueous solutions of inorganic salts of strontium, lithium and caesium.

A. Apelblat: The volume-temperature relations in systems with citrate ions.

E.S. Balankina et al.: The acoustical properties and packing factors of concentrated aqueous electrolyte solutions.

S. Boitsov et al.: Conductivity studies in benzotrifluoride.

R. Buchner et al.: Hydration of symmetrical tetra-n-alkylammonium ions.

A.A. Chialvo et al.: Ion-pair association in hydrothermal solutions by conductance experiment and molecular simulation.

F.H. David et al.: Hydration and entropy model for monatomic aquo ions.

I.A. Dibrov et al.: Computer simulation of a leaching process.

J.L. Gomez-Estevez: Thermodynamic fluctuations from the McMillan-Mayer theory of solutions in the grand canonical ensemble.

G. Hefter et al.: Viscosities of concentrated electrolyte solutions.

K. Hermansson et al.: MD+QM calculations of the OH vibrational stretching band in an aqueous aluminium(III) chloride solution.

S. Ishiguro et al.: Solvation steric effect on metal-ion complexation at the transition state.

A.M. Kirillov et al.: Physical chemistry of the polynuclear hydrolysis of aluminium and two-charged ions of 3d-metals.

R. Laenen et al.: Sub-picosecond IR-spectroscopy of aqueous salt solutions. Slowing down of the vibrational and structural relaxation of HDO.

A.S. Lileev et al.: Dielectric permittivity and relaxation in aqueous solutions of sulfates and nitrates of alkali metals in a temperature range.

I. Nezbeda: Can we understand (and model) aqueous solutions without any long-range electrostatic interactions?

G.S. Ospanova: Chemical extraction of non-ferrous and noble metals.

N.V. Pavel et al.: Combined techniques in the structural investigation of ions in solution. The symbiosis molecular dynamics – EXAFS.

I. Persson et al.: N,N'-dimethylpropylene urea. A transfer thermodynamic and structural study of its solvating properties.

M. Probst et al.: A comparison of the hydration of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ anions by molecular dynamics simulations.

T. Radnai et al.: Mass spectrometric analysis of solvate clustering compared to X-ray diffraction and theoretical results for lithium halide solutions in methanol.

L.P. Safonova et al.: Ionic dynamic in N,N-dimethylformamide at various temperatures.

T. Sismanoglu et al.: Binary and ternary metal complexes of Congo red with amino acids.

D. Spangberg et al.: Cations in mixed water / acetonitrile solutions from MD simulations.

T. Tominaga et al.: Comprehensive study of mixed micelles. Diffusion coefficients, aggregation numbers and counter ion bindings.

P. Turq et al.: Transport of water and counterions in Montmorillonite.

P. Turq et al.: Self-consistent equilibrium and transport properties in continuum solvent models of ionic solutions.

Y. Umebayashi et al.: Individual solvation numbers around first transition metal ions in N,N-dimethylformamide and N,N-dimethylacetamide mixtures.

A. Wakisaka et al.: Alkali metal chloride clusters showing primary step of crystallization.

Poster Contributions:

G. Ahn-Ercan et al.: Theoretical examination of structure and ion solvation in dioxane – water mixtures.

K. Arh et al.: Enthalpies of dilution of aqueous ionene solutions.

A.K. Baev et al.: Quantitative parameters of the copper(II) and cobalt(II) cations behavior in aqueous solutions.

A.K. Baev et al.: Metal solvo complexes – mixed hydroxides – ferrites.

J. Cerar et al.: Dependence of the molar conductivity of aqueous solutions of fullerenehexamalonates on temperature.

P. D'Angelo et al.: Recent advances in the structural investigation of ionic solutions by means of X-ray absorption spectroscopy.

J.A. Fadeeva et al.: Investigation of the system phosphoric acid – N,N-dimethylformamide as potential solvent for cellulose.

K. Fumino et al.: Pressure effects on the spin-lattice relaxation rates of deuterium nucleus for D2O molecules in alkali earth chloride aqueous solutions by NMR spectroscopy.

A.M. Gaspar et al.: Investigations of the structure of concentrated aqueous solutions of aluminium and magnesium salts in the liquid and glassy states.

G. Hefter et al.: Hydration and Na+ binding in aqueous oxalate solutions.

M. Imano et al.: MD studies of intermolecular vibrational spectra for isotopically substituted aqueous LiBr solutions.

K. Kajiwara: Solubilities in the ternary system electrolytes / sugars / water containing sodium, potassium, glucose, galactose and xylose.

Y. Kameda et al.: Neutron diffraction study on the structure of concentrated aqueous ammonium chloride solutions.

G. Keceli et al.: Adsorption behavior of strontium on rock.

A.M. Kirillov et al.: Heteropolynuclear hydroxo complexes of chromium(III) with aluminium(III) and scandium(III) in water solutions.

D. Maljkovic et al.: The influence of initial parameters on metal content in equilibrated organic phase at extraction with phosphoric extractant.

V. Nesterenko: Thermochemistry of the liquid-phase iodide-three-iodide environmentally safe redox process of processing of hydrogen sulphide-containing gases.

K.B. Nilsson et al.: Coordination chemistry of the copper(I), silver(I) and gold(I) ions in phosphites, phosphines, liquid and aqueous ammonia. A vibrational, EXAFS and 63Cu NMR spectroscopic study.

S. Pura et al.: Ion association of hexammine cobalt complexes in ethanol-water mixed solvents.

A. Salabat: Prediction of water activity in aqueous salt-polymer systems using polymer scaling laws.

M. Tomsic et al.: Conductometric study of magnesium sulphate in water from infinite dilution to saturation.

C.A. Viana et al.: Volumetric properties of lithium perchlorate and tetra-ethylammonium bromide solutions in organic aprotic solvents.

C.A. Viana et al.: Structural effects on the partial molar volume of phosphonium and ammonium salts in organic solvents.

K. Yonehama et al.: A Raman study of aqueous inorganic salt solutions in liquid and glassy states.

Ionic Liquids and Molten Salts

Invited Lectures:

H.A. Oye: Thermodynamic modeling of molten salt mixtures.

C. Bessada: Local structure and dynamics in molten salts by high-temperature NMR.

P.A. Madden: Association in ionic melts – its structural and dynamical consequences.

Oral Contributions:

I. Okada et al.: MD simulation of crystal growth from CaC12 melt.

V.A. Volkovich et al.: Oxidizing species in molten carbonates. Their generation, identification and reactions on nickel metal and oxide.

Poster Contributions:

D.N. Kagan et al.: Concentration correlation function in liquid alkali-metal mutual solutions up to 1200 K.

P. Turq et al.: Cluster analysis of HF/KF mixtures.

V.A. Volkovich et al.: Complexes of vanadium in oxidation states II to V formed in molten chlorides. An electronic absorption spectroscopy study.

Colloids in Liquids

Invited Lectures:

R. Klein: Charge-stabilized colloidal suspensions. Phase behavior and effects of confinement.

I.K. Snook: The simulation of colloidal suspensions by molecular methods.

B.J. Ackerson: Subtle order in settling suspensions.

Oral Contributions:

L. Belloni: Monte-Carlo study of specific colloidal interactions induced by surface ionic adsorption.

W. Kunz et al.: Electrical conductivity in inverse aqueous micelles in supercritical CO2.

L. Martinet et al.: Chain penetration and reverse micelle chain length. Interaction potential and phase separation in small w/o microemulsions.

H. Versmold: Viscoelastic behavior and small angle scattering.

Poster Contributions:

Z. Abbas et al.: Corrected Debye-Hückel analysis of surface complexation.

M. Bester Rogac et al.: Structural characterization of water/1-hexanol/C12E23 microemulsions by small-angle X-ray scattering.

M. Gunnarsson et al.: Surface complexation models. Determination of the inner layer capacitance from surface charge curves.

T. Yamaguchi et al.: Hydration of N-octanoyl-N-methylglucamine micelles by light scattering, small-angle X-ray scattering and molecular dynamics simulation.

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Abstracts

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Invited Contributions

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Subtle Order in Settling Suspensions

Bruce J. Ackerson
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Every physicist knows that studying the dropped ball (or apple) produced profound evolution in our conceptual understanding the universe from Aristotle, Galileo, and Newton to Einstein. What more can possibly be learned by dropping balls in this age of super-strings, photonics, and quantum encryption? However, the settling of balls in a fluid still proves vexing. When a ball settles in a fluid of infinite extent, the magnitude of the (theoretical) fluid velocity field decays as $1/r$ to leading order, where r is the distance from the center of the ball. This velocity field or "wake" produces a force on another ball placed at the distance r. The magnitude of the force being proportional to the solvent velocity also decays as $1/r$ to leading order. This hydrodynamic force decays with distance more slowly than the gravitational or Coulomb forces (which decay as $1/r^2$ and are said to have "infinite" range!). As a result the collective motion of balls at a large distance produce stronger forces on a given ball than the motion of nearby balls. This turns physical intuition inside out!

My talk will explore the effect of these long range interactions and give some examples of interesting settling phenomena including recent measurements of subtle "ordering" in well mixed "random" suspensions. Direct imaging of settling, non-Brownian, hard sphere, particles allows measurement of particle occupancy statistics as a function of time and sampling volume dimension. Initially random relative particle number fluctuations, become suppressed, anisotropic, and dependent on the average particle number. Fitting to a simple Gaussian pair correlation model suggests a minute long ranged correlation leads to strong if not complete suppression of number fluctuations. Calflisch and Luke predict a divergence in velocity fluctuations with increasing sample volume size based on random (Poisson) statistics. Our results suggest this is not a valid assumption for settling particles.

Work done in collaboration with **Professor Penger Tong** and **Dr. Xinya Lei.**
Supported by NASA and the NSF.

"Molecular liquids and their solutions interpreted in the "landscape" paradigm"

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The theory of glassforming liquids and solutions is presently in a state akin to that of solids at the beginning of the last century. when the proper manner of treating the collective vibrational modes of the substance was being worked out, and the phonon dispersion relations were being established. The distinction between liquids and solids lies in the central importance of the potential energy that changes dramatically with temperature. relative to crystals. In most solids. the defects that change the potential energy are a minor perturbation of the ground state. In liquids the change in potential energy with temperature is the dominant effect. and the one responsible for the high heat capacity, which can be more than twice that of the corresponding crystal. The problem has been to find the appropriate collective coordinates for describing the structures. of which there are some exp(23) per mole of packing units. An approach being followed by many workers at the moment is often referred to as the "energy landscape" approach. in which the excited states of the system that determine the non-vibrational potential energy are represented by minima in the potential energy lying on a multidimensional potential energy surface. The dimensionality is 3N +1 for constant volume systems or 3N + 2 for constant pressure systems.such as are studied by most experimentalists. The important things to know about this surface are the density of the configurational states for liquid and solution systems of different character (e.g strong vs fragile) and the manner in which the depths and shapes of the minima change with their energy. The different levels of the landscape that determine the liquid character are selected by prevailing temperature.

In this talk we will review the manner in which this characterization of the "landscape" is proceeding. (ii) on the one hand by theoreticians doing simulations and. on the other. by experimentalists carrying out novel experiments. Some attention will be paid to the problem of constant volume vs. constant pressure and the contrasting effect of vibrational excitations in the two cases.

Local structure and dynamics in molten salts by high temperature NMR

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Keywords : High Temperature, Nuclear Magnetic Resonance Spectroscopy, NMR, molten salts, fluorides, chlorides.

Because of their low viscosity, molten salts do not generally give glassy materials upon cooling, and the investigation of their structure by any spectroscopic methods has to be performed in situ, at relatively high temperature (up to 1020°C, in the case of fluorides).

In addition, due to their volatility and corrosiveness at high temperature, the different techniques currently used for the structural characterisation of materials, such as Raman, EPR, NMR and XAFS spectroscopies have to be specially adapted.

Recent developments of NMR spectroscopy at high temperatures allow now to investigate a great number of molten systems and to propose a more precise description of the microscopic structure of the melt in terms of different species, average coordination, or nature of first neighbours.

Due to the rapid exchange between the different bonding configurations, the NMR spectrum in the melt consists of a single, narrow, lorentzian shaped line, the position of which is quantitatively expressed by the weighted average of the individual contributions. The different local informations provided by the selective NMR observation of the various nuclei present in the system can help greatly to elucidate the structure.

The heating system developed in Orleans is based on the direct irradiation of the sample by a CO_2 laser. This system insures the heating of the sample in the NMR probe with a minimal thermal power and without perturbation of the RF coil. The design used up to 1500°C is associated with a closed boron nitride crucible that can be filled in a gloves box under dried argon. This system has been successfully used for high temperature experiments in molten fluorides or chlorides, very sensitive to moisture or oxygen and known for their volatility and corrosiveness towards a number of materials.

27th International Conference on Solution Chemistry
August 26-31, 2001
Vaals, Netherlands

MOLECULAR MODELING AND SIMULATION OF SUPERCRITICAL WATER AND AQUEOUS SOLUTIONS

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Abstract

We describe molecular dynamics simulations of supercritical water and supercritical aqueous solutions (including alkali halides and HCl) using simple non-polarizable models of water and a new polarizable model for water developed in our research group. We compare the simulation results to neutron diffraction studies. Dilute supercritical aqueous electrolyte solutions are studied by molecular dynamics to develop a microscopic understanding of ion pairing at near-critical and supercritical conditions, to determine the dissociation constant and the equilibrium constant between paired species for comparison to relevant experimental measurements, and to determine the conductance for comparison with experimental measurements. Recent examples of our work are provided in the references below.

This work has been supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. AAC's research effort is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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2. A. A. Chialvo; P. T. Cummings, "Molecular-based modeling of water and aqueous solutions at supercritical conditions," *Adv. Chem. Phys.*, **109**, 115-205 (1999).
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6. A. A. Chialvo; P. G. Kusalik; Y. V. Kalyuzhnyi; P. T. Cummings, "Applications of integral equation calculations to high-temperature solvation phenomena," *J. Statistical Physics*, **100**, 167-199 (2000).
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9. T. Driesner; P. T. Cummings, "Molecular simulation of the temperature- and density-dependence of ionic hydration in aqueous SrCl2 solutions using rigid and flexible water models," *J. Chem. Phys.*, **111**, 5141-5149 (1999).
10. S. H. Lee; P. T. Cummings, "Molecular dynamics simulation of limiting conductances for LiCl, NaBr, and CsBr in supercritical water," *J. Chem. Phys.*, **112**, 864-869 (2000).
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Theories of structural and dynamical properties of ions in discrete solvents. Application to Magnetic Resonance Imaging

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From selected examples, this review is aimed at demonstrating the ability of the molecular Ornstein-Zernike (MOZ) theory [1-6] to describe the structural, thermodynamical, and even dynamical properties of solvent molecules and solutes, and at comparing its performance with those of the numerical simulations. For liquid mixtures and for dilute solutions, we briefly recall the MOZ formalism and the approximations inherent in the various popular closure equations which are related to the hypernetted chain (HNC) diagrammatic expansion. These closures are necessary to complete the OZ relations. For selected aprotic polar solvents, with various molecular shapes and dielectric properties, the accuracy of the MOZ-HNC approximation is checked by comparing its predictions with the Monte-Carlo simulation data for simple models of unpolarizable molecules [7-9]. Then, the HNC internal excess energies and dielectric constants of polar solvents of practical interest are calculated by treating the molecular polarizability explicitly [10]. They are shown to be in good agreement with the experimental data. Firstly, for electrolyte solutions, the solvation of alkali and halide ions at infinite dilution is investigated in acetonitrile and acetone via the HNC approximation [11]. It is shown that the solvation structure around the ions is strongly influenced by the solvent-solvent spatial correlations in the pure solvent. More recent Monte-Carlo simulations of these systems are analysed and globally support the HNC predictions [12]. Turning to solutions at moderate electrolyte concentrations, the MOZ-HNC approximation is solved for a dissociated solution of cryptate K^+22 , Cl in deuterated acetonitrile [3]. The interest of the MOZ formalism to interpret neutron diffraction data and to characterize the liquid local order is discussed. Its particular ability to investigate the intermolecular potentials by fitting the force field parameters through a comparison between the MOZ and experimental spectra is emphasized.

The second part of this review is devoted to the properties of ionic species at low concentrations in water. This protic solvent is an associating liquid, for which the standard MOZ-HNC theory is only semi-quantitative [6,9]. Thus, it is simply modelled [1,4] by a system of polarizable hard spheres with embedded point electric dipoles and tetrahedral quadrupoles, and the spatial correlations between the water-like molecules are just calculated using the reference linearized hypernetted chain (RLHNC) approximation that gives theoretical dielectric constants in good agreement with experiment. For testing the relative distribution and motion of two given species in solution a particularly suitable method is the magnetic dipolar intermolecular NMR relaxation [1,4,13]. The latter is more easily measured and interpreted in the case of paramagnetic solutes which are the major source of nuclear relaxation. The various formalisms allowing to calculate the dipolar intermolecular relaxation rates in an accurate way without any adjustable parameters are briefly presented, and selected advances obtained by these NMR studies are underlined. Firstly, we show the drastic influence of the discrete nature of the water molecules on the solvent averaged Coulomb attraction between cations and anions [14]. Specific attention is directed to the ^{1} and ^{3} relaxation for the tetramethylphosphonium-nitrosodisulfonate $(CH_3)_4$ /$^\bullet$ON(SO$_3$ ^{2} attractive ion pair in heavy water solutions [15-17]. The measured relaxation rates are interpreted by assuming that the relative distribution of the two ions is given by the Boltzmann factor of their reference HNC potential of mean force and that their relative translational diffusion is described by a Smoluchowski equation accounting for this effective potential. In addition to its well-defined magnetic dipolar coupling, the free radical spin has an important hyperfine scalar interaction with the ^{3} spin. The strength of this interaction is independently measured from the paramagnetic

frequency shifts of the ^{3} resonance lines *versu* the free radical concentration. The validity of the model of interionic distribution and motion is emphasized by its accurate prediction of the ratio $T^{e}_{1n}/$ of the ^{3} longitudinal and transverse intermolecular relaxation times. Finally, we consider the paramagnetic G ^{3} ions which, because of their large electronic spin value $S = 1/$, are right in the middle of a revolutionary development in medicine: magnetic resonance imaging (MRI). Using the tetramethylammonium $(CH_3)_4$ cations as probe solutes of well-defined relative spatial dynamics with respect to the G ^{3} complexes, we show how nuclear magnetic relaxation dispersion (NMRD) studies of the $(CH_3)_4$ proton longitudinal relaxation rate provide valuable information on these complexes. For instance, the complexation of G ^{3} by nitrate anions N can be analyzed [18]. Moreover, it is possible to get a rather accurate value of the G ^{3} longitudinal electronic relaxation time [19], which is too short to be directly measurable by the presently available techniques and which partly controls the efficiency of the G ^{3} complexes employed as contrast agents in MRI medical diagnostics. The values derived from the NMRD study are in fairly good agreement with those obtained through a much more complex analysis of the EPR spectra of the G ^{3} complex [20]. Future progresses of the theory are envisaged.

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EXPERIMENTAL APPROACHES IN NON-ELECTROLYTE SOLUTIONS

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Very often physical-chemistry investigations of non-electrolyte solutions have been done along directions related to specific interests, *i.e.* understanding molecular interactions from a structural point of view or developing models for phase equilibria from thermodynamic data. In both cases experimental techniques and associated data obtained therefrom span a large variety of physico-chemical properties and also over extended ranges of temperatures.

In this context we have developed and intensively used new calorimetric techniques, particularly transitiometry, able to work at high pressures and at elevated temperatures. Data then obtained allow to give a full representation of the *pVT*-surface of investigated systems, including phase equilibria. Whenever possible we tried to couple different techniques in order to obtain in a single experiment complementary information.

Recently, we have associated calorimetric techniques with UV/Vis/IR spectroscopy, covering the wavelength range from 200 to 1300 nm, with a view to perform simultaneous *in situ* measurements on liquid systems, making use for this of optical fibers connected to a miniaturized spectrophotometer. In this way, the complex processes due to competitive interactions between simultaneous chemical and/or physical phenomena (like liquid → liquid phase separation and crystallization) can be better understood and described.

In a first series of experiments parallel calorimetric and spectroscopic measurements have been carried out. Spectra have been recorded and compared with heat effects (*i.e.* thermograms) obtained in a similar way using a calorimetric device specially designed for titration. In that case, a new differential calorimetric detector [1] has been used, working at atmospheric pressure and at temperatures up to 350 K.

In a second series of experiments the optical probe has been adapted in the high-pressure cell of a scanning transitiometer [2]. The cell being equipped with stirrer and injection devices, spectra can also be recorded together with heat effects as functions of added reactants. Tentatively the set up is being operated up to 20 MPa in the temperature range from ambient to 420 K [3].

The combination of spectrometry and calorimetry will be illustrated with selected examples

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Charge-stabilized colloidal suspensions: Phase behavior and effects of confinement

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Recent applications of nonlinear Poisson-Boltzmann (PB) theories will be reviewed. As a first case, results of an investigation of the existence of gas-liquid coexistence in charge-stabilized suspensions are discussed. It is shown that a PB-cell-model, linearized about the Donnan potential, gives rise to a gas-liquid transition, in agreement with earlier results. However, this transition disappears when the full PB equation is numerically solved for a spherical cell. Other recent applications concern situations where counterion distributions are strongly disturbed when a colloid particle approaches an interface, which may be neutral (such as air) or charged (like electrodes, glass, etc.). Two cases will be discussed: i) a spherical particle near a like-charged interface, and ii) a rodlike particle in the vicinity of an oppositely charged interface. The latter serves as a model for the adsorption of DNA on a cationic membrane. There are several contributions to the effective interaction of these particles with the interfaces, the image charge effects, the deformations of the counterion clouds of particle and interface, and for the case of oppositely charged objects, the counterion-evaporation effect.

* in collaboration with H.H. von Grünberg

Molecular fluids and solutions adsorbed in porous media: A new challenge for Integral equation theory

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Integral equation theory has experienced an enormous growth in the field of molecular fluids for the last 20 years [1], in particular within the framework of the Molecular Ornstein-Zernike theory, in which the molecular distribution functions are expanded onto the rotational invariant space to deal with the angular dependence. In this way an accurate description has been attained for all sorts of fluids composed of linear molecules and even for systems with non spherical geometries[1]. Even quite recently the effects of association have been incorporated into the formulation [2]. An important and closed related problem is posed by the behavior of a molecular fluid in the presence of a quenched random matrix. Since the formulation of the Replica Ornstein Zernike (ROZ) by Given and Stell [3] it is now possible to formulate a complete set of ROZ equations for molecular fluids adsorbed in a random matrix formed by the quenching of any given fluid. In this communication we will present the formulation of the ROZ equations for molecular fluids and for solutions adsorbed in random porous media obtained by quenching of spherically shaped particles. The predictive power of the approximation will be tested for neutral and polar particles and for neutral and charged matrices.

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Thermodynamics of solvation of small hydrophobic and hydrophilic solutes in room temperature and supercritical water

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The solvation thermodynamics of both charged and uncharged spheres in ater at room temperature and two supercritical state points are calculated from simulations. The effect of both density and temperature changes are considered. For uncharged spheres we find that the ratio of the solvation free energy to kT is density dependent but barely temperature dependent. This shows that the solvation free energy is dominated by the solvation entropy. The solvation entropy is primarily determined by the distribution of cavities within the solvent. Lowering the density has a large effect on the cavity distribution function, but changing the temperature at constant density has very little effect. For charged spheres the solvation free energy is dominated by energetics, and especially by the electrostatic interaction between the ions and the water. However differences between the solvation free energy at different state points may be determined by differences in entropy. There is a minimum in the solvation entropy versus charge curve at room temperature, but this disappears at supercritical densities. The change of solvation entropy with charge is much less for larger ions than for smaller ones at all state points.

Association in ionic melts – its structural and dynamical consequences

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Many binary systems (and their mixtures) which might be expected to be "ionic", from electronegativity considerations, are found to exhibit pronounced "covalent effects" in their condensed phase structure and dynamical properties. Theoretical work [1], has suggested that the interactions arise and are describable within the ionic model – with polarization effects playing a crucial role. In systems where they are substantial, these many-body effects promote remarkably rich changes in the intermediate-range order (IRO) of the liquid. $AlCl_3$ becomes molecular [2] on melting, $BeCl_2$ a "living polymer" of extended chains [3], in contrast to the 3-d network, glass-forming system $ZnCl_2$ [4].

When such materials are dissolved in "structure-breaking" melts (like KCl), they remain partially associated, forming more or less complex molecular ions (like $AlCl_4^-$) which persist for finite lifetimes. These molten salt mixtures then, are in a state of dynamic chemical equilibrium, with molecules breaking-up and re-forming on the pico- to nanosecond timescale. The presence of these complex ions influences, *inter alia*, the transport properties (conductivity *vs.* diffusivity), vibrational spectroscopy and the liquid structure, in the bulk and at the vapour interface. The connection between the microstructure and these particular observables, as traced through computer simulations, will be the dominant theme of the lecture.

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Whether are Hydrogen-Bonds Strengthened or Broken by Elevating Temperature and Pressure?

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Water is a typical hydrogen-bonding molecular liquid and one water molecule has about 4.4 nearest water molecules at room temperature and an atmospheric pressure. The nearest water-water intermolecular distance (r) is about 283 pm at ambient temperature and pressure, but the distance increases with decreasing *density* (practically independent of individual temperature and pressure), the increase in the water-water distance causing the expansion of the volume of water, and then, reaches a plateau value of about 290 pm in the supercritical region (see Fig. 1a). On the other hand, the number of water molecules at the nearest neighbour (N) monotonously decreases from about 4.4 under an ambient condition to about 1.7 in supercritical water (Fig. 1b). The result suggests that hydrogen bonds in water are decomposed with the decrease in the *density*, and temperature and pressure play a similar role for breaking hydrogen bonds in water.

On the other hand, hydrogen bonds in formamide, another typical molecular liquid forming three dimensional hydrogen-bonding network, are decomposed with elevating temperature, but are enhanced with the increase in pressure (NMR chemical shifts of ^{1}H, see Fig. 2a and b; ○: -C-H and ●: -N-H). Formamide forms a head-and-tail linear and ring dimer mixed structure in the network and a hydrogen bond in the former is stronger than that in the latter (Fig. 3). Moreover, the ring-dimer has a more compact form than the linear structure, and thus, the former is more preferable under high pressure, while the latter is predominantly formed at high temperature.

Thus, the formation of hydrogen bonds is dependent on molecular structures and the structure in the condensed phase. Such a consideration should be taken into account at discussions of structures of proteins and other hydrogen-bonding biomolecules.

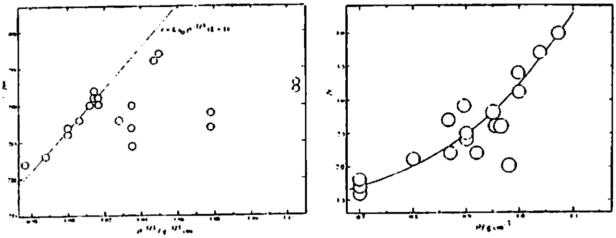

Fig. 1 a (left): r plotted vs. $\rho^{-1/3}$, b (right): N vs. ρ.

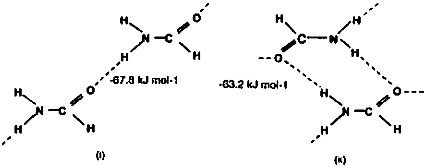

Fig. 3. Energies of H-bonds in linear and ring dimer.

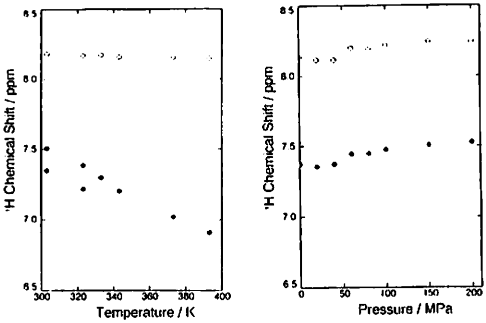

Fig. 2 a (left): ^{1}H chemical sift vs. T, b (right): ^{1}H chemical sift vs. p.

Thermodynamic Modelling of Molten Salt Mixtures

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In ionic crystals cations are surrounded by anions and *vice versa*. This feature can also be applied for molten salts, the socalled Temkin model. A mixture can be considered the sum of a cation mixture and an anion mixture, and the mixing entropy the sum of the cation entropy and the anion entropy. By statistical thermodynamics the ideal entropy of the compound C_mA_n becomes:

$$a^{id}_{C_mA_n} = X^m_C X^n_A$$

where X_C is the cation fraction and X_A the anion fraction.

The consequence is that the activity of NaCl in a 0.9 NaCl - 0.10 NaBr mixture is equal to 0.90, while the NaCl activity in 0.90 NaCl - 0.10 KBr is 0.81. Deviation from activity can be described by activity coefficients using the well known regular solution model:

$$a_{NaCl} = X_{Na^+} X_{Cl^-} \cdot \gamma_{NaCl}$$

The concept of defined structural species, so-called complexes, was earlier considered doubtful in molten ionic mixtures, as the entities are not separated by a solvent. The complex concept has, however, found to be very useful and entities predicted by thermodynamics have later been identified by Raman and IR spectroscopy. An early example was the phase diagram of the system KCl-$MgCl_2$ on the KCl-side. Assuming the entity $MgCl_4^{2-}$ and placing the magnesium ion in the anion lattice then gave a perfect description of the liquidus line on the KCl side. Another example is the equilibrium

$$AlF_6^{3-} = AlF_4^- + 2\,F^-$$

which describes the phase diagram around the Na_3AlF_6 composition.

Binary and ternary mixtures of the system aluminium chloride - alkali chlorides will be used to demonstrate the power of such models. In spite of that the aluminium chloride activity varied over 10 orders of magnitude, the mixture could be described satisfactory by the assumption of the complexes $AlCl_4^-$ and $Al_2Cl_7^-$. Modelling also helped to describe properties not measured or properties that hardly could be determined experimentally.

Water at Interfaces

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The organization of water at the interface with another material, whether liquid, solid, or gas, is strongly influenced by the ability of that other material to participate in hydrogen bonding with water molecules and by the topography of the interface. Such organization and interactions, in turn, are critical to the interfacial free energy associated with the presence of the interface. A particularly important case is that of water at hydrophobic surfaces, which presents itself in the contexts of fluid-fluid interfaces, fluid-solid interfaces, and in biomacromolecular contexts. In this presentation, results obtained from computer simulations at a variety of interfaces will be discussed from this perspective, in order to elucidate the influence of the interface on water structure and energetics at a molecular level. The examples to be considered include extended solid hydrophobic and hydrophilic surfaces, surfaces of single folded proteins and those involved in protein subunit assembly, the sequestered surface of an enzyme active site, and the interface between liquid water and supercritical carbon dioxide.

The Simulation of Colloidal Suspensions by Molecular Methods

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ABSTRACT

Most simulations of the dynamical properties of particle suspensions use the method of Brownian Dynamics (BD) in which the system is treated as a collection of heavy colloidal particles of mass M suspended in a background medium, or bath, of light particles of mass m. The latter is treated as a continuum by means of macroscopic hydrodynamics. This approach has several limitations. Firstly, BD methods give no detailed information on the structure and dynamics of the background medium in the presence of the colloidal particles. Secondly, the BD method is based on the Langevin equation which is a limiting case of the fundamental, molecular Liouville equation for the combined system of colloidal and bath particles. The derivation of this limit has only been carried out at equilibrium and when M/m is infinite. This poses at least two questions viz what are the equations of motion in a non-equilibrium steady state and at what finite value of M/m is the BD method applicable? The latter question is of current practical concern as it is important to know if BD methods are applicable to suspensions of nano-particles.

We have recently used two approaches to address these questions which we will outline here. Firstly, we have derived a molecular Generalised Langevin Equation (GLE) for a system in an external field in the steady state. This equation has been used to give a molecular based derivation of a Langevin equation for a suspension in a shear field.

Secondly, we discuss the results of Molecular Dynamics simulations of a two component system of particles having different masses and interacting according to a simple pairwise additive force law. Thus, both colloid and bath particles are treated on the same footing. Equilibrium and non-equilibrium results in a shear field will be presented. In particular, these simulations show that the Brownian limit is approached for relatively small values of M/m but that the exact value at which this is achieved depends on the relative sizes of the colloidal and bath particles.

Corresponding States in Electrolyte Solutions

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Properties of ionic fluids such as phase equilibria, electrical conductances and dielectric behavior are reviewed and discussed on a corresponding-states basis, using the properties of the hard sphere ionic fluid (primitive model) as a guide. Special attention is given to states at low reduced temperatures which correspond to solutions in solvents of low dielectric constant, where ion pairing and the formation of higher ion clusters becomes important. Making use of room temperature molten salts, one can investigate the properties of such solutions up to the fused salt. This introduces new features associated with the restructuring of the ion population from associated states to the pattern of a fully dissociated molten salt. In solvents of low dielectric constant this process is usually accompanied by a liquid-liquid phase separation in which the solution decomposes into a dilute, almost non-conducting solution and a highly conducting salt-rich phase. The experimental results are discussed with regard to the current state of the theory. Examples for the effect of additional short-range specific interactions upon the various properties are shown.

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Oral Contributions

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POSITIONAL CORRELATIONS IN CONCENTRATED AQUEOUS SOLUTIONS OF INORGANIC SALTS OF STRONTIUM,LITHIUM AND CAESIUM

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The existence of a local order around the strontium cation and around the sulphate anion in concentrated aqueous solutions of strontium chloride and bromide and of sulphates of lithium and caesium was investigated by X-ray diffraction. A liquid type quasi-close-packing seems to be an adequate model for solutions of strontium salts. The interpretation of the profile of the X-ray intensity in diffraction patterns obtained with solutions of salts with polyanions using alike molecular models is discussed. Previous investigations are reexamined [1,2,3,4,5]

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LOCAL ORDER IN CONCENTRATED AQUEOUS SOLUTIONS OF SALTS CONTAINING IONS OF DIFFERENT VALENCIES. X-RAY DIFFRACTION INVESTIGATIONS.

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In X-ray diffraction investigations of the structure of concentrated aqueous solutions of barium and magnesium chloride and bromide a local order involving shells of ions and water molecules around the ions of highest valence beyond the direct contact seems to be necessary to interpret the profile of the intensity given by the structure factor. Previous analysis of results obtained for aqueous solutions yttrium, lanthanum and indium salts are discussed [1,2,3,4].

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THE VOLUME-TEMPERATURE RELATIONS IN SYSTEMS WITH CITRATE IONS.

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Densities of dilute aqueous solutions in the 0.003 - 0.1 molal concetration range of citric acid, tri-sodium citrate, tri-potassium citrate, tri-ammonium citrate, di-sodium hydrogen citrate, sodium dihydrogen citrate, and potassium dihydrogen citrate were determined at 5 K temperature intervals from 278.15 K to 343.15 K. Measured densities were used in the evaluation of the apparent molar volumes, cubic expansion coefficients, the apparent molar expansibilities and the second derivatives of the volume with respect to temperature. These parameters were expressed as a function of temperature and concentration. The influence of dissociation equilibria on the volume -concentration - temperature relations in the systems with citrate ions is also discussed.

Phase Equilibria of Binary Mixtures of Halogenated hydrocarbons

Vapour-Liquid equilibria of Fluorinated Hydrocarbons

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Mixtures of Fluorinated hydrocarbons exhibit strong non-ideal behaviour leading to the formation of low boiling azeotropes, as a consequence of high activity coefficients.
Vapour-Liquid Equilibria (VLE) of the nine binary mixtures of C_6H_5F, $C_7H_5F_3$ and $C_2H_2F_3OH$ were measured using a dynamic circulation still technique at 100 kPa.
The experimental results were well represented by the Wilson and UNIQUAC models.
Excess refractive indices n_D^E of the above binary mixtures were obtained by an Abbe -type refractometer.
Excess enthalpies H^E of binary mixtures were measured using a C80 Setaram calorimeter.
Excess volumes V^E of binary mixtures were measured using an Anton-Paar electronic densimeter
The experimental excess properties at 298.15 K of the studied mixtures (X^E, x) were very smooth.

Solid-Liquid Equilibria of N,N-dimethylacetamide with 1-propanol, 1,2-dichloroethane and dichloromethane

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Crystallization is an important separation process in several industrial fields, where solid-liquid equilibria (SLE) phase diagrams of multi-component mixtures of organic solutions should be known.
In predictive thermodynamic studies such G^E models and Group Contribution (UNIFAC) Methods, SLE data of eutectic systems are used to cover the low temperature range for better fit and more reliable estimation of group-interaction parameters and contribute successfully in the development of software tools used for the synthesis and separation processes.
Thermodynamic properties of mixtures formed from N,N,-dimethylacetamide are poorly studied and their experimental data are scarce in the literature.
This work reports SLE experimental data of N,N-dimethylacetamide +1,2-dichloroethane, + dichloromethane, +1-propanol measured using the visual technique at the pressure 101.3 kPa.
The reduction and correlation of the results were thermodynamically consistent.
The phase diagrams $(T, x)_p$ of N,N-dimethylacetamide with 1,2-dichloroethane or 1-propanol were well represented by the NRTL and the modified UNIFAC (Dortmund) models. While N,N-dimethylacetamide with dichloromethane gave a distinct compound at equimolar composition.

THERMODYNAMIC AND SPECIFIC INTERMOLECULAR INTERACTIONS IN SOLUTION OF NON-ELECTROLYTES WITH PENTACOORDENATED CARBON ATOM

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During the last decade considerable progress has been made in solutions of element organic compounds with alkyl ligands of non-transition elements. In these lecture we are discuss specific intermolecular interactions in non-electrolyte solutions of element organic compounds with participation of methyl group of alkyl ligands in which carbon atom is consist of pentacoordinated condition. We are discussed the thermodynamic data dependence of $\Delta_{vap}H^{o}(T)=f(x)$ and carry out thermodynamic analysis of structural changes in solutions of binary systems of alkyl compounds with isostructural molecules of compounds and with different disposition of deviation from Raoult law on isotherms of vapour phase. The dissociation energies of different kinds of specific intermolecular interactions using thermodynamic properties of evaporation process of the solution components with discerned of number of intermolecular bonds have been determined. The numerical significance of the dissociation energies of specific interactions in solutions occupies intermediate position between energy of hydrogen bond in water and ammonia. We laid down rows changing of value of energy of specific interaction in solvates of different systems with isostructural molecules of components. The value of energy of the same type of specific interaction in different solvates of system depends on role of molecules of component – solvated agent or solvated molecules have been established.

Using thermodynamic properties and energy of specific interaction in solutions we substantiated:

- Solutions of element organic compounds of the same homologous series of with neighbouring homologue are dissimilar with ideal condition;
- Negative deviation from isotherm of vapour phase fulfils condition if average interaction energy of molecules with solvated agent in solution is less than in components. This case realize if there is negative deviation from additive value on dependence of $\Delta_{vap}H^{o}(T)=f(x)$;
- Fulfillment of Raoult law on isotherm of vapour pressure is not reflect ideal condition of solution because of $\Delta_{vap}H^{o}(T)=f(x)$ dependence has negative deviation from additive value.

Probing the Solvation Shell of Organic Molecules by Intermolecular ^{1}H NOESY

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When a species is dissolved in a mixed solvent, the composition of its solvation shell may be different from that of the bulk solution, which is known as preferential solvation (PS). We have probed the PS of neutral and charged organic species in binary solvent mixtures from intermolecular ^{1}H 2-D NOESY measurements.[1-3] We will firstly present results pertaining to the overall solvation of neutral solute molecules, *i.e.* phenol and nitroanilines in various binary solvent mixtures (water/CH_3CN, water/DMSO, water/alcohols, CH_2Cl_2/Et_2O, cyclohexane/THF), and the dependence of the PS of phenol on the relative concentration of the two cosolvents, as well as PS in the cavity of α-cyclodextrin.

Secondly, we will discuss the local features of the solvation shell of polar neutral molecules possessing a hydrophilic functional group and a linear alkyl (hydrophobic) chain in binary solvent mixtures. It will be shown that the extent of enrichment in the solvation shell of the organic cosolvent is consistent with the solute structure.

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Ab initio molecular dynamics simulation of liquid formic acid.

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We studied, using first principles methods, structural, and dynamical properties of liquid formic acid. This investigation employed gradient-corrected density functional theory based on the BLYP functional. The system calculated consisted of 32 formic acid molecule in a periodically replicated box. Computed structural properties are in good agreement with our new neutron diffraction experimental data, as well as X-ray data. Computed dynamical properties (diffusion coefficient, reorientational time) reproduce experimental data as well.

The optimized equilibrium and saddle point geometries of formic acid and formic acid formiat anion dimer are in good agreement with previous ab initio quantum chemical calculations. Finally, proton transfer in formic-acid-formiat anion has been investigated with this method.

THE ACOUSTICAL PROPERTIES AND PACKING FACTOR OF CONCENTRATED AQUEOUS ELECTROLYTE SOLUTIONS

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The analysis of concentration dependencies of acoustical properties of aqueous electrolyte solutions has been carried out in a wide range of concentration. Among the large of number systems, including binary and multicomponent aqueous solutions of salts, it has single out some systems (~20) where linearity a quadrate of a velocity (u^2) down to saturation is observed. For solutions of halogens and nitrates of alkali metals the linear extrapolation of u^2 to 100 % of a saline component yields a value of u^2 for the melted, supercooled salt. The magnitudes of partial molar compressibility of salts at infinite dilution ($\overline{K}_{2,s}^{0}$) were shown to be in a good agreement with results obtained from concentration extrapolation of experimental data of compressibility coefficient and density in dilute solution (with infinitely small amount of salt). The interpretation of concentration acoustical dependencies from 100% water to 100% salt is provided on the basis of structural scheme including bulk water (1), water in hydration shells (2) and ionic clusters (3) in two concentration bands. The main principle of connection of these subsystems is the complementary organization of configuration (1), (2), (3). In framework of this scheme the analytical expressions for a velocity in a hydration shells in the first, second concentration bands were deduced and the condition of linearity of u^2 from 100% water to 100% salt was obtained. It was explained the deviation from linear concentration dependence in case of concentration changes of hydrophilic, hydrophobic hydration and complex formation of ions. It was deduced the expression for calculation of nonlinear acoustic parameter of solutions, using volumetric-elastic experimental data. It was estimated the magnitude of molar volume and coefficient compressibility of hydration water.

The nonlinear acoustic parameter (B/A) is strongly structure sensitive. It was offered the theoretical method of evaluation packing factor of solutions and initial components (pure water and melted supercooled salt) using parameter (B/A) in framework developing structural scheme. The packing factor is introduced as one of the main parameters of relationship of structure of solutions and acoustical properties.

The work was supported by the Russian Foundation of Basic Research.

Monte-Carlo study of specific colloidal interactions induced by surface ionic adsorption

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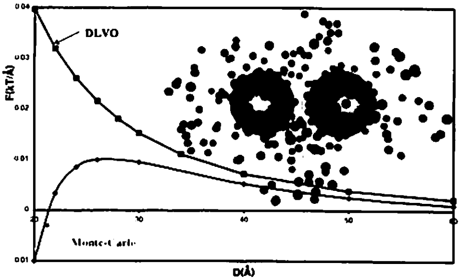
Surface ionic adsorption and colloidal interactions are studied within the "Charge Regulation Primitive Model" (CRPM). The motor for the adsorption is a short-range sticky colloid-ion potential that mimics the chemical or physical affinity of the ions for the colloidal surfaces. As opposed to the traditional Primitive Model, the resulting colloidal surface charge is not fixed, nor uniform but becomes mobile, heterogeneous, fluctuating and coupled to that of neighboring particles. The CRPM is exactly solved using grand-canonical Monte-Carlo simulations around two colloids immersed in an electrolyte. The local ionic profiles and the colloidal forces are calculated for different size, salinity and affinity parameters. At the point of zero charge (same affinity for cations and anions), a pure attraction appears which is due to the coupling between the two fluctuating charges. The force-distance law behaves as $-\exp(-2\kappa r)/r^2$ where κ is the screening constant and r is the separation. Away of the point of zero charge, this attraction strengthens and may overcome the standard DLVO repulsion $+\exp(-\kappa r)/r$ at short separations (figure). Complex coupling between adsorption and electrostatics are responsible for this behavior. The Monte-Carlo data are compared to previous HNC integral equation theories and to Poisson-Boltzmann analysis. This attraction which is related to the chemical nature of the ions through their adsorbing properties could explain some specific, non generic effects (those non simply explained by the ionic valency) observed for instance in the protein crystallization process.



Conductivity Studies in Benzotrifluoride.

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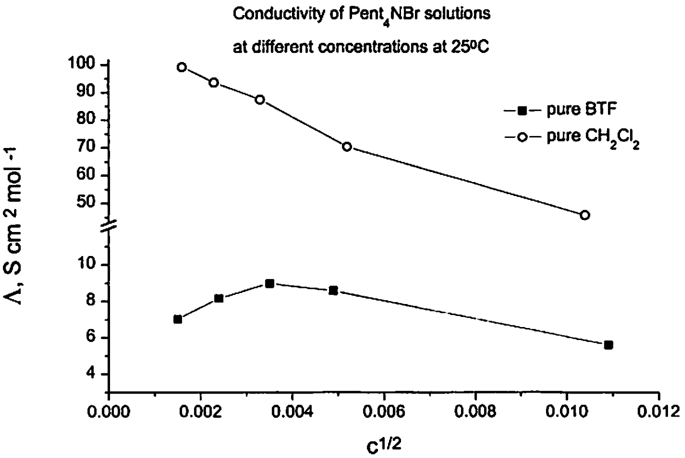
Benzotrifluoride (1,1,1-trifluoromethylbenzene, BTF) has in the last decade been used extensively as a solvent for organic reactions. A high dipole moment, 2.56 D, a considerable permittivity, ε=9.3, and some donor properties, DN=18 kcal/mol, combined with its aromatic properties cause BTF to be an efficient solvent for many substrates. The solvent is most stable; only in the presence of hard Lewis acids will some decomposition take place. The fairly low boiling point, 102.2 °C, the low toxicity and its extreme reluctance to absorb water are additional reasons for the recent popularity of this solvent.

Since a number of onium salts are quite soluble in BTF we have performed a conductivity study on several salts in this solvent. A plot of the molar conductivity of $Pent_4NBr$ in BTF and in the isodielectric solvent CH_2Cl_2 is shown below:



Much to our surprise all the examined salts showed a maximum in the plots at ~10^{-5} M as shown for $Pent_4NBr$ above; c_{max} being slightly but distinctly dependent upon the size of both the cation and the anion. To the best of our knowledge this phenomenon has not previously been observed in any solvent. The form of the Λ-$c^{1/2}$ plots inevitably prevents Λ^0 and the degree of dissociation, K_d, to be determined.

These observations seem to indicate a unique case of solvent-enforced ion-pairing caused by the preference of the BTF molecules to form "*trans*-dimers" in the pure liquid. These dimers appear to be destroyed by even minor impurities as f. ex. dissolved salts. Theoretical calculations have been used to arrive at stabilization energies for the various possible geometries of the BTF dimers.

Hydration of Symmetrical Tetra-*n*-alkylammonium Ions

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Hydrophobic effects due to the interactions of non-polar molecules or moieties with water are relevant in many fields of chemistry and biology. An important aspect is the hydration of the solute, *i.e.* the solute-induced change of the structure and dynamics of the surrounding solvent, which can be probed by dielectric relaxation experiments. This technique yields information on the impact of the solute on the co-operative dynamics of the hydrogen-bond network of water. From the determined effective hydration numbers inference on the structure can be gained.

Symmetrical tetra-*n*-alkylammonium bromides (TAABr), $(C_nH_{2n+1})_4NBr$, $n=1$ - 5, were selected as model compounds for the investigation because they permit to probe the transition from "normal" ion hydration, effective for $(CH_3)_4N^+$, to hydrophobic hydration typical for $n \geq 3$. The contribution discusses the changes of the dielectric relaxation behaviour of water induced by the dissolved electrolytes. At 25°C pure water exhibits two dispersion steps. The low-frequency process with a relaxation time of τ_{s1}=8.33ps covers 97% of the total dispersion in the microwave range. It is attributed to the co-operative relaxation of the H-bond network. Additionally, a small-amplitude high-frequency dispersion with τ_{s2}=0.34ps can be detected. These relaxation processes are also observed for the investigated solutions. Similar to simple inorganic electrolytes $(CH_3)_4NBr$, $(C_2H5)_4NCl$, and $(C_2H5)_4NBr$ exhibit a decrease of S_{s1} with increasing electrolyte concentration, c. Interestingly, $\tau_{s1}(c)$ significantly increases, *i.e.* the co-operative dynamics is slowed down, whereas inorganic electrolytes affect $\tau_{s1}(c)$ only weakly. Both effects are also observed for tetrapropylammonium bromide and the higher homologues. But additionally a low-frequency dispersion step with a $\tau \approx 20$ps emerges and its amplitude rapidly increases at the cost of S_{s1}. It is shown that this new relaxation process can be attributed to "slow water" in the hydration shell of the TAA cations, which differs considerably from "bulk" water in its dynamics.

Ion-Pair Association in Hydrothermal Solutions by Conductance Experiment and Molecular Simulation

What have we learnt and what can we expect?

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Knowledge of the properties of supercritical aqueous mixtures is essential to the understanding of the dissolution, transport, and precipitation of salts in many natural environments and industrial processes. The characterization of these hydrothermal systems requires knowledge of the equilibrium constants for the solubility and ionization processes. In particular, the thermodynamic description of many natural and industrial processes including volcanic vapors, hydrothermal vents, steam power generation and supercritical water oxidation, relies on the availability of accurate data for the thermodynamic behavior of aqueous electrolyte solutions.

The dissociation of MX in aqueous solutions (where M includes $H3O^+$, Cu^+, Na^+,Li^+, and X includes Cl^-, OH^-) has been studied extensively by calorimetric techniques, electrical conductance, and solubility measurements (Mesmer et al., 1991). Yet, the thermodynamic properties of these aqueous solutions, especially those at high temperatures and low densities, are still the matter of some debate, in that the dissociation constants determined from solubility data appear to be at odds with those from conductivity measurements (Chialvo et al., 2000; Ho et al., 2000a; Ho et al., 2000b). These discrepancies highlight the intrinsic challenges behind the accurate measurements of electric conductivity in low-density, dilute, and extremely corrosive aqueous systems, the likely existence of additional species not taken into consideration in the treatment of solubility data, and consequently, the need for improved experimental methods and more sophisticated modeling techniques. The fundamental driving force for speciation reactions in the competition between solvent-solute, and solute-solute interactions in solution. Molecular-based approaches to ion solvation show great potential in the quest for a fundamental understanding of ion solvation, by guiding the interpretation of experimental data, assisting in the assessment of their consistency, and connecting the microscopic and macroscopic properties of interest in a rigorous, unambiguous fashion (Chialvo and Cummings, 1999).

As part of a wider ongoing investigation on high-temperature ion solvation and complexation, in this work we focus our attention on ion-pair association in hydrothermal systems. We report on our latest molecular-based studies of ion-pair association at precisely the same corresponding states as those from our own conductance experiments with a flow-through cell. This comparison allows us to test the reliability of the intermolecular potentials involved, before we proceed with the simulation studies at conditions unattainable by current experimental methods, such as at lower density and higher temperature. The knowledge of the ion association behavior under these experimentally inaccessible conditions is becoming one of the most important goals of the high temperature aqueous chemistry, because this region can yield fundamental information regarding ion-pair solvation that is essential for the proper modeling of these mixtures (Sverjensky et al., 1997).

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Hydration and Entropy Model for Monatomic Aquo Ions.

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The hydration model we had proposed (1) is extended to aquo species having covalent bond. In this case, the experimental cation-oxygen distance, δ, is shorter than the calculated data obtained with an ionic model. The observed decrease is used to evaluate the effective charge of covalent species. We discuss the evaluation of the coordination number N and the number of water molecules in a second hydration shell, H, the radius, R_w, of the water molecule in the two hydration shells and give useful expressions for their determinations. Since hydration entropy and entropy of the aquo ion S_{aq} can be deduced from the derivative of the free hydration energy $\Delta G(hyd)$ versus temperature, we propose an entropy model, considering five terms corresponding to the derivative versus temperature of the distance δ, the numbers N and H, the polarisability and the quadrupolar moment of the water molecule. The two proposed models are tested for ions with charges −1, +1, +2 and +3. The calculated $\Delta G(hyd)$ and $S°_{aq}$ data are in excellent agreement with available experimental data (accuracy of the order or better than 1%). We have shown that the models can be extended to tetravalent ions. They have been applied successfully to halides, alkalis, alkalino-earths, trivalent and tetravalent lanthanides and actinides and "3d" ions.

Finally, according to the relationships between the main characteristics of the aquo ions, we conclude that characteristics of an aquo ion can be defined to a great extent by two main parameters: crystallographic radius and cation-oxygen distance, which are both measured with accuracy by X-rays diffraction and X absorption spectroscopy. Moreover, the consideration of the proposed equations could be used to predict or precise interesting characteristics such as N, q_{eff}, H or δ.

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COMPUTER SIMULATION OF A LEACHING PROCESS

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Computer simulation of real chemical and hydrometallurgic processes is a difficult problem due to complexity of systems, great number of participants, lack of initial thermodynamic information, first of all, activity coefficients of soluble species. Nevertheless, such calculations allow to reject in advance deadlock ways, minimize number of expensive and complicated experiments and see main tendencies of researches, which can be confirmed by a laboratory experiment.

In the paper we should like to give an example of such simulation that was used for increase of zirconium output to a solution in the leaching process of eudialithe concentrate and, at the same time, improvement of sedimentic properties of silica gel.

Most of natural zirconium minerals are poorly soluble in acids what hinders their leaching. The only exception is eudialithe, which is incongruently soluble in all mineral acids with forming of silica sediment and solution containing Zr, REM, Ca, Mg, etc. But the forming silica is present as a non-filtered colloid sol and output of Zr to the solution does not precede 60% due to formation of $ZrSiO_4$ (zircon).

Thermodynamic computer calculations by a "Gibbs" program, based on minimization of total Gibbs energy, showed that fluoride ions are to increase the zirconium output into any acid solution. The calculations were made for leaching of eudialithe by nitric and sulfuric acid containing 6.0 equivalents per liter with silica and zircon as anticipated precipitates and all zirconium complex ions as anticipated aqueous species.

The main Zr species in the acid solutions were proven to be $Zr(NO_3)^{3+}$ and $Zr(SO_4)_2^0$, after addition of fluorides with molar ratio F:Zr   3.0 the main species are ZrF_2^{2+}. The calculated Gibbs energies of main leaching reactions at 363K are following:

$$ZrSiO_4 + 4H^+ + NO_3^- = Zr(NO_3)^{3+} + SiO_2 + 2\ H_2O;\ \Delta G^0 = 61.74\ kJ/mol$$
$$ZrSiO_4 + 2H^+ + 2HSO_4^- = Zr(SO_4)_2^0 + SiO_2 + 2\ H_2O;\ \Delta G^0 = 13.37\ kJ/mol$$
$$ZrSiO_4 + 2H^+ + 2HF^0 = ZrF_2^{2+} + SiO_2 + 2\ H_2O;\ \Delta G^0 = 2.53\ kJ/mol$$

As one can see, solubility must grow in the sequence: < H_2SO_4 < HF. The results of analyses of solutions on Zr (mole / l) after leaching of an eudialithe concentrate by nitric and sulfuric acids containing 6.0 eq / l in presence of different additions of NaF confirmed the computer results:

F : Zr, mole/mole	0	1	2	3	6
HNO_3	0.043	0.054	0.062	0.066	0.071
H_2SO_4	0.044	0.056	0.064	0.070	0.070

Of course, the results of computer calculations coincide with experimental ones not precisely, differing each other sometimes up to 50%, but the tendencies are quite adequate.

Modeling of Supramolecular Ordering in Mixtures: Structure, Dynamics and Properties

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The results on modeling supramolecular organization of the molecular mixtures, selforganized by specific bonding, and unified description of the series of thermodynamic, dielectric, optic, kinetic properties [1,2] have been reviewed.

The hierarchy of the models of supramolecular species mixtures has been considered. The methods for estimating the contributions of intermolecular forces to thermodynamic functions of pure solvents and mixtures have been developed. The methods for describing the structure, composition, dipole moment, and polarizability of polyvariable as regard to structure and composition of supramolecular species are discussed. Interrelations between thermodynamic functions (Gibbs energy, enthalpy, entropy), dielectric permittivity, optic (refractive index and its fluctuation derivatives, defining Rayleigh light scattering), and kinetic coefficients of mixtures, and microscopic characteristics of supramolecular species, are presented. These models include the mixtures with complex types of supramolecular ordering due to specific bonding and macroscopic properties, defined by different molecular characteristics.

Models of the systems of polar associating substance in nonpolar and polar inert and solvating solvent like mixtures alcohols with hydrocarbons, halogenated hydrocarbons, ketones, taking into account the linear and cyclic aggregates have been considered as a particular example.

Aggregates in liquids, including tens of molecules, were established on the basis of analysis of a set of properties of nonelectrolytes (alcohols, amides, etc.), and their mixtures with non-polar and polar inert and solvating solvents have been established. Data on the structure and thermodynamics of supramolecular aggregation in the wide ranges of the state parameters (concentration, temperature) are presented. The results have been analyzed in terms of the integral and differential parameters of aggregation. The comparing the methods developed with the another ones, e.g., computer simulation [3], are given.

The development of dynamic models for supramolecular reorganisation, intermolecular transitions, and energy transfer during thermal molecular motion in liquids, fluctuation and relaxation (acoustic, dielectric, optic) phenomena by extended thermodynamic models of systems with internal variables of the different tensor dimension have been outlined.

The macroscopic manifestations of the supramolecular organization in physicochemical properties of liquids are discussed. The problem concerning the design of liquid materials with defined physicochemical properties on the molecular-structural level have been outlined.

Acknowledgements: This work was supported by the Russian Foundation on Basic Research (projects 00-15-97346 and 01-03-32051).

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The Complexation in Mixed Water-organic Solvents

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Points of view as to how to interpret data on equilibriums of a complexation in mixed water-organic solvents have been subject to critical consideration. In our approach it is necessary to define and divide such terms exactly as a chemical form in a solution with the levels of its detailazation and medium. The standardization of the condition every detailed ingredient, which participates in the equilibrium, impossible without a strictly fixed medium for the conducting research. In this method it is necessary to use a molar scale of concentration (including water as a component of the equilibrium), that makes it simple to move from one level of detailazation to another in order clearly interpret the effects of the medium.

The multiple data by equilibriums of complexation in mixed water-organic solvents (MS) was analysed according to the aforesaid point of view. With regard to this analysis it is necessary to begin from the dependencies $\lg\beta_n$ of $\lg[H_2O]$ as opposed to any others (for example, from the molar part of co-solvent with the quantity inverted by dielectric permeability). These dependencies are linear with a tangent of inclination equaling the dentate ligand when in the process we only factor in dilution. In the case of the positives deflection from the dependencies in the system the process is carried out with the release of a large quantity of water molecules, which restructure from an octahedron to a tetrahedron or flat quadrate. In the event of a negative deflection in the system these is the possibility that the molecules of an organic ingredient will enter into the inner co-ordinate sphere of the central ion, or interact with co-solvent molecules and the ligand, or simultaneously form inner and outer sphere complexes.

These positions have been illustrated in multiple examples of our literary data.

Modeling of Excess Molar Volume of Acetonitrile with Amine Using the Prigogine-Flory-Patterson Theory

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In this work, experimental data of excess molar volumes of acetonitrile + (diethylanine or s-butylamine) as a function of composition, under atmospheric pressure and at 288.15, 293.15, 298.15 and 303.15 K, have been used to test the applicability of Prigogine-Flory-Patterson Theory[1-5]. The PFP theory includes three contributions to explain the thermodynamic behaviour of liquid mixtures: (i) the interaction contribution which is proportional to the X_{12} parameter; (ii) the free volume contribution which arises from the dependence of the reduced volume upon reduced temperature as a result of the dependence between the degrees of expansion of the two components and (iii) the P^* contribution which depends both on the difference of internal pressure and of reduced volumes of the components. Our results have shown that the interaction contribution is the most important contribution to describe the excess molar volumes of the systems studied.

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THERMODYNAMIC FLUCTUATIONS FROM THE McMILLAN-MAYER THEORY OF SOLUTIONS IN THE GRAND CANONICAL ENSEMBLE

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The original treatment of the McMillan-Mayer (MM) theory of solutions was made in the framework of the Grand Canonical Ensemble [1] Posterior developments and practical applications of the theory have focused heavily on the virial expansions of the osmotic pressure and/or activity coefficients[2].Even thougth that the MM theory has been related with the modern statistical mechanics of liquids [3],the complete development of the thermodynamics from the Grand Canonical Partition Function Ξ_{MM}, is still lacking.The purpose of this work is to advance in this direction by obtaining new results for the thermodynamic properties of the solution derivable from Ξ_{MM}.Next,the corresponding statistical fluctuations can be deduced.Some examples will be presented showing the applicability of the expressions that emerge as a result of treatment of systems in osmotic equilibrium in the macrocanonical ensemble.

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Viscosities of Concentrated Electrolyte Solutions

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The concentration dependence of the viscosities of unassociated binary electrolyte solutions in water is generally smooth, even up to very high concentrations. Nevertheless, this apparently uncomplicated behaviour is extraordinarily difficult to model even using empirical equations.

We have found that a relatively simple empirical expression of the type:

$$\log(\eta/\eta_o) = Bc + Dc^2$$

with

$$B = B_1 + B_2t$$

$$D = D_1 + D_2t$$

is able to fit viscosity data with good precision for a variety of electrolytes up to high concentrations ($0 \leq c \leq 12$ M) over a wide range of temperatures ($5 \leq t \leq 150$ °C).

Viscosities of *mixed* strong electrolyte solutions at constant ionic strength are reasonably well accounted for by assuming simple pro-rata additivity analogous to Young's rule behaviour. Departures from additivity appear to be largely related to the differences in the viscosities of the (binary) end member solutions.

MD+QM Calculations of the OH Vibrational Stretching Band in an Aqueous Aluminium(III) Chloride Solution

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Abstract

The OH stretching vibrational band has been calculated by an 'MD+QM' approach for the water molecules in the first hydration shell of the Al^{3+} ion in a dilute $AlCl_3$ aqueous solution. Molecular Dynamics-generated geometrical snapshots provided the molecular positions, which were subsequently used in ab initio calculations of charge-embedded ion-water clusters at the HF and B3LYP levels. The ion-water clusters which were treated quantum-mechanically were $Al^{3+}(H_2O)_6(H_2O)_x$ (x=2 or 3), where a few water molecules from the second hydration shell were included. 60 oscillators were selected from the MD dumps, and anharmonic vibrational frequencies were computed from the ab initio-generated potential energy curves. Density-of-states bands as well as infrared-intensity-weighted bands are presented.

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Solvation Steric Effect on Metal-ion Complexation at the Transition State

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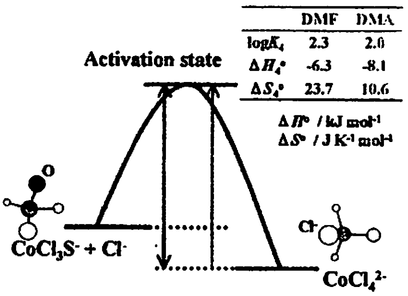
Solvation steric effect plays an important role in metal-ion complexation in non-aqueous solution. We have so far studied solvation steric effect in *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA) and their mixtures from thermodynamic and structural viewpoints. The halogeno complexation is enhanced in DMA relative to DMF owing to solvation steric effect of metal ions in DMA. This is mainly due to the enthalpy contribution. On the basis of these facts on the thermodynamic solvation steric effect, we then extended our work on the solvation steric effect at the transition state. Cobalt(II) ion forms a series of mono- to tetrachloro complexes in DMF and DMA. The metal-ion is tetrahedrally four-coordinated in the tri- and tetrachloro complexes, and the rate of the reaction, $[CoCl_3(solvent)]^- + Cl^- = CoCl_4^{2-}$ + solvent (solvent = DMF and DMA), were measured by rapid-scan spectrophotometry over a wide-range of temperature. It found that the rate is significantly slower in DMA than in DMF, and this is due to the larger enthalpy of activation in DMA. The activation enthalpy values are negative in both the solvents, suggesting the associative mechanism, and the value in DMF is significantly more negative than that in DMA. This indicates that solvation steric effect operates extensively in the transition state.. On the basis of the enthalpies of transfer of $CoCl_3^-$, $CoCl_4^{2-}$ and Cl^- from DMF to DMA at the ground state, the enthalpy of transfer of the activated species from DMF to DMA was evaluated. Here, we will discuss the more detailed mechanistic aspect of solvation steric effect at the transition state.



	DMF	DMA
$\log K_4$	2.3	2.0
ΔH_4°	-6.3	-8.1
ΔS_4°	23.7	10.6

ΔH° / kJ mol^{-1}
ΔS° / J K^{-1} mol^{-1}

Fig.1. Thermodynamic parameters of formation of $CoCl_4^{2-}$ in DMF and DMA.

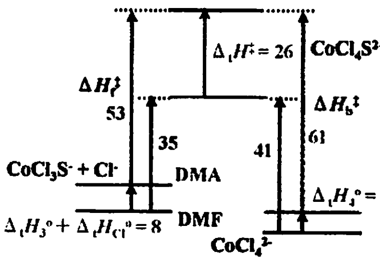


Fig.2. Enthalpy diagram for the formation of $CoCl_4^{2-}$ in DMF and DMA.

PHYSICAL CHEMISTRY OF THE POLYNUCLEÁR HYDROLYSIS OF ALUMINIUM AND TWO-CHARGED IONS OF 3d-METALS

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Also the common hydrolysis of metal ions has been extensively studied, the process of heteronuclear hydroxo complex formation in water solutions containing several metal ions and in particular Al(III) with two-charged 3d-metal ions is studied insufficiently. There are practically no data on thermodynamics, kinetics and mechanism of this process. At the same time without knowledge of the certain physicochemical magnitudes it is impossible to solve in the full many problems of geochemistry, ecology and biochemistry, adsorption, catalysis and synthesis of new inorganic materials. In this connection the results of all-up study of the metal ions cohydrolysis in the Al^{3+}-M^{2+}-NO_3^--H_2O (M = Co, Ni, Cu, Zn) system are esteemed, and the correlation between obtained physicochemical parameters are discussed at the report.

The basic areas of prevalence of the aqua-, monohydroxo- and polynuclear hydroxo complexes and transferring of them into the hydroxide precipitate both in simple systems and in solutions containing several metal ions have been established on the basis of the distribution diagrams of different aquahydoxo forms in the dependence from pH and neutralization degree ($[OH^-]/[M^{n+}]$). The defining role of the mono hydroxo forms of Al, Zn and aqua forms of Co, Ni, Cu on the polynuclear hydrolysis was detected. The correlation between quantity of the polynuclear forms, a neutralization degree and equilibrium pH value was found out.

The integrated constants of polynuclear hydrolysis and stability constants of formed hydroxo complexes are determined at the different Al^{3+}:M^{2+} ratios. The influence of M^{2+} ions on the heteropolynuclear hydrolysis is quantitatively estimated. The kinetics is learnt and the mechanism of this process is offered. The activation energies testifying of kinetic advantage of formation of the heteronuclear fragments in comparison with two homohydroxo polymers fractions at the expense of asymmetry of formed intermediate complexes with hydrogen bridges are determined. The thermodynamic parameters (ΔH°_{298}, ΔS°_{298}, ΔG°_{298}) of the polynuclear hydrolysis of Al^{3+} at the presence of 3d-metals are determined and their arguing from stands of an electronic structure of metal ions, the complexation mechanism, formation and stability of intermediate fragments, influence of the enthalpic and entropic factors is held. The analysis of all learnt Al^{3+}-M^{2+} systems has shown that the formation of heteronuclear Al-Cu fragments is followed by the least energy handicappings at the expense of the Ian-Teller effect.

Study of hydrogen bonds network in water-alcohol mixtures at ambient, sub- and supercritical condition.

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The hydrophobic hydration associates with the anomalous thermodynamics of transferring a solute into the water. The maximum of heat capacity for some of the alcohol-water mixture is well known phenomenon. In this report we examine heat capacity behavior as function of concentration for water – methanol and water tert-butanol mixtures at different parameter of state.

The molecular dynamics simulation has been employed for study of these phenomena. The hydrogen bonds networks have been extensively studied at different conditions using statistical geometry approach. The results shows clearly for water-methanol solution the simultaneous occurrence of hydrophobic and hydrophilic hydrations leads to strengthening of solvent structuredness at concentration of heat capacity maximum compare with other concentrations and even with more hydrophobic tert-butanol – water mixture at the same concentration region. The origin of this effect is discussed in report.

Diminishing of hydrophobic effect relative to ambient conditions has been analyzed and found that hydrophobic hydration diminishes slightly at the concentration of C_v maximum and drastically for the other concentrations. The competition between the structure breaking effect of the temperature increase and the structure making tendency of the decrease in density is a possible explanation for this phenomenon. This competition leads to a transition from a hydrogen bonded network to hydrogen bonded clusters. The formation of clusters with a strong tetrahedral arrangement of the water molecules near the critical temperature leads to an increase of the height of the first peak in the O-O RDFs, to relatively high average number of hydrogen bonds for a short concentration range.

WATER-ORGANIC MIXTURES AT NORMAL AND HIGH PRESSURES. THERMODYNAMIC PROPERTIES AND STRUCTURE

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It's known that water-organic mixtures are widely used in modern technologies and play the important role in biochemical processes. The study of P-V-T-x properties of solutions gives the most complete characteristics of substances state and allow to calculate all thermodynamic properties. In our laboratory investigations of thermodynamic properties of binary water-non-electrolyte systems both at normal and high (till 100 MPa) pressures was carried out. The next organic compounds were used as co-solvents: mononatomic alcohols (C_1-C_3), amides (formamide, N-methyl-, N,N-dimethylformamide, hexamethylphosphorictriamide, acetamide), nitriles (acetonitrile), ketones (acetone), cyclic ethers (propylene carbonate). The changes of thermodynamic properties of mentioned mixtures in dependence of composition, temperature and pressure are discussed in report.

On example of water-N,N,dimethylformamide system the influence of pressure and temperature on thermodynamic properties are discussed. The contrary influence of temperature and pressure on specific volume of this mixture are discovered. For all that on dependencies V=f(x) at less DMFA concentrations (x~0,05) and high pressures observed the maximum, which increase at low temperatures. This behaviour is explained by P,T influence on stabilisation aqueous tetrahedra structure with small addition of DMFA. By basis of analysis of coefficients of pair-wise interactions, second virial coefficients and their derivatives by pressure and temperature are shown that the association between N,N-dimethylformamide molecules is increased with pressure growth. The action of temperature is unequally. To P=500MPa the increasing of temperature the DMFA-DMFA interaction are intensified, over 50Mpa – loosens. On basis of change of $\partial\beta_{22}/\partial P$, as hydrophobic criterion, are shown, that hydrophobic interactions prevalence in water – DMFA system. It increases with the growth of pressure and with the decreasing of temperature.

The relation between the structures and thermodynamic parameters is the important problem of solution theory. Molecular dynamic (MD) yields information on atomistic level. MD simulation of thermodynamic properties based experimental results will yield least qualitative trends of modeled thermodynamic variables. The MD simulation of water-methanol mixtures has been applied for study anomalous behaviour some physico-chemical properties of low concentrated non-electrolyte solutes in water. On the basis of calculation of the potential of mean forces, the radial function of distribution and parameters of H-bond network the causes of anamalous are discussed.

The results discussed lead to the following conclusions: Molecular dynamics simulations of the dilute water – methanol solutions using flexible and rigid models have shown that both potencial models give a qualitatively similar picture. Both potential models show the maximum of heat capacity in the region of the low concentration of methanol. In the case of the flexible models these effects are slightly weaker than for rigid potentials. Within the rigid models the H-bonds are energetically stronger than for the flexible ones, because the charges on the sites of SPC/E and H1 models are larger than those of the BJH based models. It is concluded, therefore, that the reason for anomalous behaviour of the thermodynamic functions in the region of the dilute aqueous methanol solutions are methanol- methanol associations. Another important result is the cluster formation of the methanol molecules around aqueous tetrahedra, which are found to be quite stable and consist of three to four molecules.

This work was supported by RFBR, grant N 98-03-33237a and N 99-03-32064.

ELECTRICAL CONDUCTIVITY IN INVERSE AQUEOUS MICELLES IN SUPERCRITICAL CO_2($scCO_2$)

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Supercritical CO_2 is today a well-known fluid which is widely used in basic research and in industry. This is because $scCO_2$ is not toxic, not inflammable and chemically inert. However, a major drawback for broader application of this interesting fluid is the fact that it has only a low solution capacity for polar components. In particular, water can only be dissolved in small amounts and even this is only possible by using fluorinated and toxic surfactants to a large extent. Nevertheless, to go further on, it is important to know the structure and the physico-chemical properties of such ternary systems: Water–$scCO_2$– surfactant.

During the last three years, we built up an equipment that allows the study of inverse aqueous micelles in $scCO_2$ in a temperature range from 5 to 60°C and in a pressure range from the critical pressure (about 70 bars) up to 500 bars. The micelle formation can be detected by means of UV-VIS-spectroscopy. To characterize the systems in more details, we recently equipped our high presssure cell with an platine electrode device in order to carry out electrical conductivity measurements.

We focused our studies on ternary systems $scCO_2/H_2O$/ClPFPE-NH_4 (Fluorolink 7004) at 35°C and with constant mass ratios H_2O/surfactant and we determined the conductivity of the system as a function of surfactant concentrations at different pressures.

At small surfactant concentrations the conductivity is low and further decreases with increasing surfactant concentration up to a flat minimum. This behaviour can be explained by means of the charge fluctuation model [1] yielding an average droplet radius of about 40 Å, a value which is in agreement with small-angle neutron scattering results of PFPE-microemulsions [2].

By further increasing the surfactant concentration the conductivity sharply increases up to a value which is more than 100 times higher than the initial value. Finally, an inflexion point is observed which is typical of a percolation behaviour. The conductivity as a function of the volume fraction of the surfactant can be described with characteristical exponents around the percolation threshold. These exponents are in agreement with the dynamic percolation model [3] of highly mobile microemulsion droplets in the supercritical phase.

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CL PFPE Fluorolink

Sub-picosecond IR-spectroscopy of aqueous salt solutions: slowing down of the vibrational and structural relaxation of HDO

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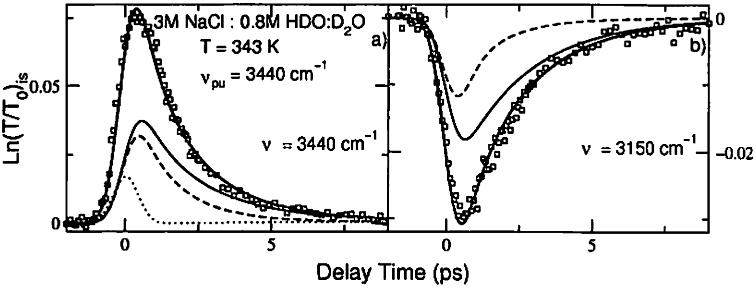
Transient IR-spectroscopy with sub-ps pulses[1] is demonstrated on aqueous salt solutions. A low concentrated solution of HDO:D_2O is investigated where the OH-group act as a local probe for the strength of the hydrogen bonds towards the surrounding deuterated water molecules. This offers the possibility to determine the lifetime T_1 of the OH-stretching vibration in aqueous salt solutions as well as the effective reorientational time constant of the investigated OH-dipole and the time constant for structural relaxation.



Typicall data are shown above for a 3M NaCl in 0.8M HDO:D_2O solution (343 K) and excitation at the center of the OH-band. While probing at the excitation frequency (a) three signal contributions are seen: coherent artefact (dotted line), HDO close by (thin solid line) and more distant (dashed line) to the salt ions. Vibrational lifetimes are derived from probing of the 12-transition within the excited-state absorption (b). From numerically fitting of the data (thick solid line in the Fig.) we found by adding of salts to the isotopic water mixture a significant lengthening of T_1^{OH} from 1 ps[2] without any salt up to 2.7 ps (NaCl)[3]. Simultaneously reorientation of the probed OH-dipole of HDO molecules in the vicinity of the salt ions slows down to 10 ps (NaCl) at room temperature.

This is explained by the disturbance of the hydrogen-bonded network in water due the presence of ions. Detailed investigations are performed with variation of the cations and anions giving further insight into the impact of ions on the dynamics of the OH-group.

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DIELECTRIC PERMITTIVITY AND RELAXATION IN AQUEOUS SOLUTIONS OF SULFATES AND NITRATES OF ALKALI METALS IN TEMPERATURE RANGE

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The aqueous solutions of nitrates and sulfates of alkali metals are studied with use of the method of dielectric spectroscopy. The temperature dependencies of complex dielectric permittivity of lithium, sodium, potassium and cesium nitrates and sulfates solutions are investigated at frequency range 7-25GHz in a wide concentration interval for temperatures 283-313K. The parameters of the dielectric relaxation process are determined: static dielectric constant (ε_s), relaxation time (τ), parameter of distribution of relaxation times.

The features of hydration and structural - kinetic changes in numbers of alkali metals solutions are established on the basis of the obtained parameters. The differences between the dilute and concentrated solutions are found. The dielectric constant of solutions decreases at increase of concentration of dissolved salts at all cases. The identical order of decreasing of ε_s for nitrate and sulfate solutions is observed (Li > Na > K > Cs) that corresponds to differences of a ionic hydration. The changes of ε_s for sulfate solutions are stronger, than for nitrate solutions (at the same cations). The temperature changes of ε_s decrease with the growth of salt concentration and at some cases the sign of temperature dependence of ε_s changes in comparison with pure water. The distinctions in change of orientation mobility of water molecules characterized by values of dielectric relaxation time connected with a negative and positive hydration of ions in nitrates and sulfates solutions. In initial concentration range the relaxation time decreases with increase of concentration in the case of nitrate solutions. The variations of τ in solutions of different compositions are insignificant. The changes of τ for sulfate alkali metals solutions have principle differences. The addition of Li_2SO_4 results to the increase of τ and, accordingly, to the decreasing orientation mobility of water molecules in solutions, while the addition of Cs_2SO_4 causes the decrease of relaxation time. The following order of changes in a number of sulfate solutions is observed: $Li > H_2O \geq Na \geq K > Cs$. Concentration changes of τ are more expressed at lower temperatures, both for nitrate solutions and sulfate solutions. The values of enthalpy of activation of a dielectric relaxation are calculated from temperature dependencies of τ. This parameter, describing a connectedness of a net of H-bonds, also differs for solutions of sulfates and nitrates of alkali metals.

Thus, the distinction of influence of anions on the dielectric relaxation characteristics in aqueous solutions of electrolytes that connected with their different hydration is established.

This work was supported by the Russian Foundation of Basic Research

DIELECTRIC RELAXATION AND STRUCTURAL-KINETIC CHANGES IN AQUEOUS NONELECTROLYTE SOLUTIONS

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The relation between dielectric relaxation, structural effects and elementary molecular-kinetic processes in aqueous solutions is considered. The experimental investigation of microwave dielectric properties of nonelecrtolyte and weak electrolyte solutions (mono- and polyatomic alcohols, amides, urea and its derivatives, HMFT, ketones, aldehydes, DMSO, acetonitril carbonic and other acids, D_2O, H_2O_2 etc) in 7-120 or 7-26 GHz range at 5-50, 10-40 or 15-35°C were carried out (~40 systems). We worked out the systematics and determined the changes that are connected with hydrophobic and hydrophilic hydration of polyfunctional molecules. Nonadditivity of changes of dielectric relaxation characteristics is a result of the mutual influence of polar and nonpolar groups of the same or different molecules. Structural breaking or structural making effects that take place when nonelectrolyte molecules act on the water H-bond net can be explained using the concept of the geometrical complementarity between configurations of the structures of the polar molecule, its first coordination sphere, intermediate layer and tetrahedral balk water. The geometrical models are used to pick out the three-dimension accordance in binary solutions. It is shown that the stabilization of water structure under the polar group influence occurs only when solute particle forms configurations of hydrate sphere that correlate with the initial water configurations (H_2O_2, HF, D_2O, etc).

The mechanism of elementary movements of water molecules in solution is analyzed on the basis of experimental data and semi-phenomenological confined rotator/ extended diffusion or "hybrid" theoretical scheme. The absorption spectra and the spectra of complex dielectric permittivity at centimeter, millimeter, and sub-millimeter ranges for the aqueous nonelectrolyte solutions (in the case of acetone, DMSO, acetonitril) are described. A new method is proposed to study a molecular nature of hydrophobic and hydrophilic hydration in solution in wide range of concentrations at the level of elementary orientational processes. It allows to separate the contributions of different groups of polifunctional molecules with hydrophobic and hydrophilic hydration.

The work was supported by the Russian Foundation of Basic Research

Towards a prediction scheme for hydration properties of aqueous hydrocarbons up to the critical region of water

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Hydration properties of aqueous hydrocarbons at elevated temperatures describe evolution of interactions between a hydrophobic solute and water at conditions where mechanic and dielectric characteristics of solvent are strongly changing. These properties are of high practical interest for petroleum chemistry and geochemistry due to the direct connection of the Gibbs free energy of hydration with the Henry's law constant, which is essential for solubility and air-water partitioning calculations. It is therefore useful to look for a convenient scheme for predicting the hydration properties of hydrocarbons as a function of temperature and pressure.

A considerable progress has been achieved over the last decades in description of thermodynamic properties of aqueous solutes at the standard state of infinite dilution up to the critical region of water. New equations have been proposed[1] inspired by the theories of near critical solutions and the fluctuation solution theory (FST) which are modern alternatives to the semi-empirical Helgeson-Kirkham-Fowers model[2]. The development of these new approaches was guided by experimental data in the critical region of water resulting mainly from calorimetric and volumetric experiments performed over the last ten years or so.

Sedlbauer et al.[3] have proposed recently a semi-theoretic hydration model based on FST and derived a related group contribution scheme[4]. At the same time we have collected most available high temperature data on aqueous hydrocarbons resulting from phase equilibrium, calorimetric and volumetric measurements that are useful for calculation of hydration properties. This allowed establishment of an extensive database of Henry's law constants, enthalpies of hydration, and heat capacities and volumes at infinite dilution that was used for calculation of group contributions for hydration properties of aqueous alkanes, alkenes, cycloalkanes, and aromatic hydrocarbons. The thermodynamic basis of the group contribution scheme will be outlined and examples of the predictions will be shown.

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Preferential Solvation in Completely Miscible Aqueous Co-solvent Binary Mixtures at 298.15 K.

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The Kirkwood-Buff integrals for 18 completely miscible aqueous co-solvent binary mixtures have been re-calculated from thermodynamic data. The volume-corrected preferential solvation parameters derived from them are presented. Also presented are these latter quantities for 15 additional such mixtures, for which the volume correction has not been applied previously.

The preferential solvation parameters provide direct information concerning the self-interaction of the water, the mutual interaction of the water and the co-solvent, and the self-interaction of the co-solvent over the entire composition range. The latter interactions at infinite dilution derived from these integrals and parameters are then discussed and related to the hydrophilicity and electron pair donicity of the co-solvent..

The systems studied include aqueous hydrogen peroxide, methanol, ethanol, 1- and 2-propanol, 2-methyl-2-propanol, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, ethane-1,2-diol, glycerol, 2-methoxyethanol (at 313 and 343 K), 2-ethoxyethanol, 2-butoxyethanol, 2-aminoethanol, N-methyl- and N,N-dimethyl-2-aminoethanol, tetrahydrofuran, 1,4-dioxane, acetone, formic, acetic, and propanoic acids, piperidine, pyridine, acetonitrile, formamide, N-methyl- and N,N-dimethylformamide, N-methylacetamide, N-methylpyrrolidin-2-one (at 303 K) hexamethyl phosphoric triamide, dimethylsulfoxide, and tetramethylenesulfone (at 303 K).

CHAIN PENETRATION AND REVERSE MICELLE CHAIN LENGTH : INTERACTION POTENTIAL AND PHASE SEPARATION IN SMALL W/O MICROEMULIONS

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Some extractant molecules used for ion selective extraction, form reverse aggregates in oil. These oligomeric aggregates have an aggregation number between 2 and 10 molecules, depending on conditions. These aggregates are demonstrated to be small apolar core including water, polar heads and extracted ions, surrounded by a sterically stabilizing layer made by the three apolar chains per molecule. Combined Small angle X-ray scattering and Small angle neutron scattering on the same sample give the access to the volume of the aggregate in solvent and the extent of the polar cores. These polar cores are shown to interact via sterically stabilized Van der Waals interactions. This interaction is characterized via temperature using determination of the structure factor S(q) by scattering. We show that this experimental method allows to rationalize the effect of varying the oil solvent chain length (penetrating oil) and the apolar extractant chain length. The attractive potential between these reverse micelles is determined versus solvent chain length from hexane to hexadecane and for surfactant chain length from 10 to 18 carbon atoms.

Effects of Polar Groups on Hydrophobic Hydration Probed by ^{1}H and ^{13}C NMR Chemical Shifts and Frequencies of C-H Stretching Vibration Bands

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In the original proposal of hydrophobic hydration, hydration of nonpolar solutes such as hydrocarbons and rare gases was interpreted in terms of the reorganization of hydrogen bonds among water molecules, where hydrophobic hydration refers to the way a nonpolar solutes affects the local structure of water in its immediate environment. The study of hydrophobic hydration, however, has been made complex by the facts that the solubilities of nonpolar solutes in water are too small to be used in usual experimental techniques and that the thermodymanic properties characteristic of hydrophobic hydration of nonpolar solutes were observed as well as for organic solutes with a polar group. In order to study hydration of alkyl moiety, the effect of interaction with water and the polar group on hydrophobic hydration should be taken into consideration in analysis of results. Using solutes with hydrophilic moiety and changing and extrapolating their polarity to zero may be profitable for this purpose.

Thus in this paper, we compare the effects of >S=O, >C=O, -CONH-, and -O- groups in organic solutes on the concentration dependence of chemical shifts for water protons and the frequency of C-H stretching vibration bands of the solutes in aqueous binary mixtures. We measured chemical shift by the external double reference method.[1-3] By the method, the chemical shifts measured at different concentrations or temperatures are all expressed on a unified scale to be compared strictly with each other.

We propose a mechanism of hydration of the hydrophobic moiety, in which hydrogen-bonding basicity of the polar groups is a decisive factor for the hydration.

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CAN WE UNDERSTAND (AND MODEL) AQUEOUS SOLUTIONS WITHOUT ANY LONG-RANGE ELECTROSTATIC INTERACTIONS?

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A computer simulation experiment is conducted to study to what extent long-range Coulombic interactions are indispensable when modeling aqueous solutions of electrolytes. A simple molecular model, which accounts explicitly for the molecular structure of water but which does not incorporate any long-range Coulombic interactions, is employed. The solvent is primitive water (EPM5-4 model) and the solute molecules are hard spheres interacting with the interaction sites of the water molecule by means of either repulsive (like-charge interaction) or attractive (unlike-charge interaction) short-ranged triangular-well tails. The structural changes (structure breaking and structure enhancement) which take place in an infinitely dilute solution upon 'charging' the solute are studied, in terms of the correlation functions and of the orientational distribution functions and of the average binding energy of the water molecules around the solute in terms of their dependence on the solute-water oxygen distance. The thermodynamic property reflecting these changes is the residual entropy. This quantity is found to exhibit a double maximum, in agreement with the findings for a realistic counterpart of this simple model that employs long-ranged Coulombic interactions.

Ultrasonically Induce Birefringence of Polymer Solutions

By

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The most physical properties of polymer solutions are caused by the local segmental motions and polymer chain distribution in solutions. If the ultrasonic waves irradiate in polymer solutions, the sinusoidal orientation order can be produced by the sinusoidal velocity gradient and the birefringence phenomena will be observed. For the phenomena in polymer solutions, Peterlin has proposed a theory at 1950 and first experimental data has been reported by Jerrad et.al(1962).

Reentry, we derived the expression for the ultrasonically induced birefringence of polymer solutions based on the modem theory of polymer dynamics and compared with Peterlins's theory.

At the same time we started to measure the ultrasonically included birefringence of polymer solutions, that is polystyrene in toluene solutions, in the frequency range of several ten to hundled MHz as a function of ultrasonic power, concentration of polymer solutions and molecular weight of polymer in solutions.

The ultrasonic power dependence of ultrasonically induced birefringence of polymer solution in MHz region are well reproduced quantitatively by our new expressions. In MHz region, ultrasonically induced birefringence increased with incasing concentration in solutions, but did not depend on the molecular weight. This experimental results are very interesting and strongly indicate that ultrasonically induced birefringence will mainly concern the local segmental motions. In the presentation, we will discus ultrasonically induce birefringence of polymer solutions in more details.

MD Simulation of Crystal Growth from $CaCl_2$ Melt

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We have previously studied crystal growth of NaCl from its supercooled melt by molecular dynamics (MD) simulation[1]. To our knowledge, this was the first MD trial of crystal growth from an ionic melt. In the present study we have extended the method to $CaCl_2$ whose crystal has a distorted rutile structure; a=623 pm, b=642 pm and c=419 pm at room temperature.

Crystal growth on the (001) and (100) planes has been studied. In most cases 6x6x11 Ca^{2+} and 72x11 Cl^- (totally 1188 ions) were disposed in the perfect crystal in the basic cell. Periodical boundary conditions were imposed in the x- and y- directions but not in the z-direction which is open to a vacuum. The upper 7 layers were melted, while the lower 4 layers were kept at the crystalline state. After some runs for equilibration between the two phases, crystallization on the interfacial plane was started by setting the temperature of both phases as a given (supercooled) one; for example, 1000 K, while the (experimental) m.p. is 1055 K. During the whole simulation the ions on the first (bottom) layer was kept unmoved so that the crystalline phase was stable. The Gilbert-Ida potentials whose parameters were presented by Umesaki and Iwamoto[2] were used. For calculation of the coulombic forces and potentials the two-dimensional Ewald method was used.

The growth rate on the (001) plane seems to be higher than that of other planes such as (100) and (110) planes. This is presumably because in the (001) system both Ca^{2+} and Cl^- are present on every layer and in this respect the structure resembles that of the melt phase. On the (001) plane growth rate of Cl^- is slightly higher than that of Ca^{2+}. The growth rate is lower than that of NaCl ({100} plane) by about two orders of magnitude. In the case of $CaCl_2$ the 3 ions have to crystallize simultaneously to keep the local charge neutrality.

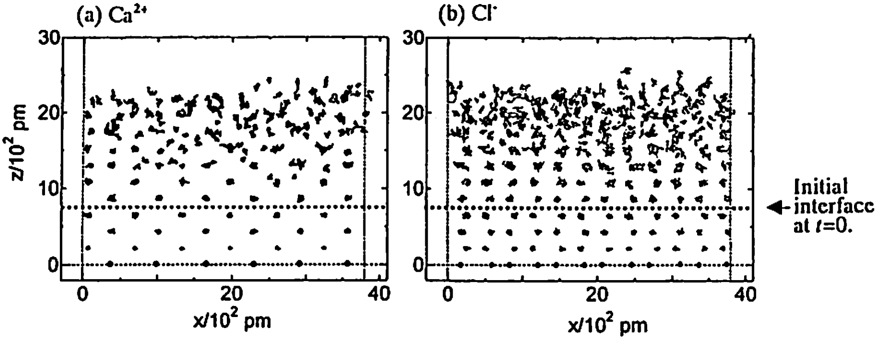

Fig. 1. Trajectories of Ca^{2+} and Cl^- projected on the x-z plane in the (001) plane system; T=1000 K, t=366-368 ps, and (NVT) ensemble.

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CHEMICAL EXTRACTION OF NON-FERROUS AND NOBLE METALS

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Now perspective and effective technology of extraction of metals is the heap leaching based on transferring of metal from mineral raw materials in a solution, in situ. The most suitable mineral raw materials are: sub-standard, lean ores, deposits with small reserves, technogenic raw (slimes, slangs, tails of dressing and gold extraction plants, etc.). Advantages of technology of a heap leaching of metals are: high productivity, low capital and exploitational expenditures, less composite system of environmental protection.

Depending on the different factors: the shapes of a presence of useful components, attendant devices, composition of adjacent strata etc., developed and the technologies with usage of effective, accessible, ecologically safe chemical reagents of a different nature (inorganic, organic) in a wide interval of pH (from 1 to13), permitting are recommended to receive high extraction non-ferrous and noble metals (98-99 %) in a solution in weak conditions (atmospheric pressure and ambient temperature). The indexes of extraction of noble metals in solution with usage of developed non-cyanide solvents are higher than in cyanide solvents under lesser cost and toxicity. The indexes of extraction of non- ferrous metals in developed combined chemical solvents also are higher than in sulphuric acid traditionally used at a heap leaching of copper. It is necessary to mark, that the developed and offered solvents for noble and non-ferrous metals specially effective for sulphide refractory ores, for which one cyanide solvents and sulphuric acid are unacceptable owing to low indexes on extraction. The thermodynamic parameters of dissolution of copper and gold are determined.

The concentrating non-ferrous and noble metals from technological solutions after a heap leaching will be carried out on sorption technology on synthetic and natural sorbents of an organic and inorganic parentage from local raw. The synthetic sorbents are polymers from monomers available in Kazakhstan. The adsorptive properties of local natural sorbents beforehand by special fashion handled and prepared to process, are determined by feature of a constitution of frame. The new sorbents are characterized by ability to bind ions as in cationic, and anionic shapes depending on a type of a ligand and requirements; have high mechanical tensile strength permitting to reuse without decreasing of the performances of sorption process; are inconvertible against low temperatures; acidic and alkaline conditions; at cost synthetic sorbents, as well as commercial, but on quantity of capacity on gold on 1-1,5 about greater; Cost of natural sorbents on 1,5-2 about lower, than commercial, at similar capacity. The optimal conditions of obtaining of synthetic and natural sorbents with given properties for extraction non-ferrous and noble metals (Cu, Au, Ag, Pt, etc.) are determined. Is shown, that on a surface the polymer - metal complex will be formed. The kinetics of a sorption both desorption of copper and gold is investigated. The further processing of eluates with obtaining of marketable products is carried out by electrolysis. The cathodic copper containing 99,99% Cu is obtained. The wastes of a heap leaching of non-ferrous metals are utilized as raw material for building materials. Developed technologies of obtaining of bricks, tiles are recommended.

The developed technologies of chemical extraction non-ferrous and noble metals from mineral raw materials with usage of new non-toxic solvents and accessible sorbents are tested in pilot scale heap leaching on various genetic and industrial types of ores and technogenic wastes of dressing plants, protected by the patents of Republic of Kazakhstan. The ecological, economical and practical efficiency of recommended technologies is shown.

Dynamics of equilibrium establishment of the inhomogeneous solution methanol-hexane near the separation critical temperature

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Investigations of height and temperature dependence of equilibrium and non-equilibrium values of the refractive index gradient dn/dz(z,T) of the binary solution methanol-hexane were carried out under gravity close to the phase interface ($T < T_c$) by refractometry methods. The dynamic equation of the non-equilibrium state of the substance was proposed on the basis of assumption about correspondence of non-equilibrium height distribution dn/dz(z,t) to the equilibrium value dn/dz(z, ΔT) for certain temperature $\Delta T = T - T_c$.

Combined techniques in the structural investigation of ions in solution: the symbiosis Molecular Dynamics-EXAFS

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A general theory of ionic solutions can be developed only with the accurate knowledge of their solvation structure. Several experimental techniques have been used to determine the solvation structure of ions in solutions. Among them, X-ray absorption spectroscopy (XAS) is particularly well suited for the investigation of the ion-solvent and ion-ion associations. The advantages of this method are its atomic selectivity, which allows a better extraction of the structural information related to different coordination shells around the selected atom, and its sensitivity to dilute solutions.

Our knowledge of disordered structures is often limited to the pair distribution functions g(r) probed by diffraction techniques. The extended X-ray absorption fine structure (EXAFS) spectroscopy offers the opportunity to extract information on higher order correlation functions describing the ion-solvent associations. The presence of these functions appears in the XAS spectra as multiple scattering (MS) effects whose quantitative analysis allows the presence of angular correlation with the solvent molecules to be detected.

In the standard EXAFS analysis the coordination of the photoabsorber is usually defined, in the harmonic approximation, by means of Gaussian shells. This procedure shows severe limitations in the case of ionic solutions, where the ion-solvent pair distribution functions are asymmetric. The neglect of this asymmetry in the EXAFS data analysis leads to significant errors in the determination of the coordination parameters [1,2]. The main contributions to the EXAFS signal are generally due to the single scattering and MS effects which are present in the first solvation shell.

The aid of other structural or computational techniques may be essential to define the interval of variation used to model the pair and higher order correlation functions in an EXAFS fitting procedure. A new strategy for the EXAFS data analysis has been developed in our laboratory [3] and it has been checked on several ions in aqueous and non-aqueous solutions [4]. It has been demonstrated that in the presence of many coordination shells around the photoabsorber atom, g(r) models obtained from Molecular Dynamics (MD) simulations can represent an essential starting point for the EXAFS analysis. The MD g(r) is splitted into an asymmetric first peak and a long distance tail. This peak is modeled with a gamma-like distribution function which depends on four parameters, namely the coordination number, the average distance, the distance mean-square variation and the skewness. The parameters of the asymmetric peaks are refined in order to achieve the best fit to the experimental spectrum. The EXAFS data analysis has been performed using the GNXAS program [5].

Several ions give rise to non-regular coordination in solution and in these cases the presence of well-defined three-body correlations can be individuated on the basis of the MD calculations. The full set of parameters associated with the (g(r1,r2,θ)) distributions can be determined and the corresponding MS signals can be included in the EXAFS data refinement [6]. Note that when MD simulations are not wide of the mark, the fitting process is similar to a minimisation with constrained parameters.

Instead of using the MD g(r)'s in the the EXAFS data refinement, Palmer and al. [7] have used a set of clusters extracted from MD simulations as input for the calculation of individual EXAFS spectra. These spectra are averaged together to obtain a theoretical EXAFS spectrum that is compared to the experimental one.

The two MD-EXAFS methods will be compared and relevant cases of ion-solvent coordination determined by combining MD and EXAFS techniques will be illustrated.

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N,N'-Dimethylpropylene Urea
A Transfer Thermodynamic and Structural Study of its Solvating Properties

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N,N'-Dimethylpropyleneurea, DMPU, is a relatively bulky molecule requiring much more space at solvation of ions than most other oxygen donor solvents. The bonding characteristics of DMPU are similar to those of sulfoxides and formamides, $D_S = 34$. The transfer thermodynamics of monovalent cations from water to DMPU show that almost all ions are slightly more strongly solvated in DMPU than in dimethylsulfoxide, DMSO, and the heats of transfer are of the same order of magnitude in both solvents. The similar transfer thermodynamics of monovalent ions to DMPU and DMSO indicate similar configuration of ions in these two solvents. This has also been proven for the monovalent ions silver(I) and thallium(I).

The coordination number of DMPU solvated metal ions is in many cases lower than found in most oxygen donor solvents due to the bulkiness of the DMPU molecule. A survey of the structure of ca. 20 *N,N'*-dimethylpropyleneurea solvated metal ions in solution will be presented. The complex formation ability of a metal has been found to be strongly dependent on the configuration of the solvated metal ion. Nickel(II) forms only weak complexes with the halides in DMSO, where the solvate is octahedrally six-coordinated, while significant complex formation is found in DMPU where the solvate is five-coordinated.

A Comparison of the Hydration of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ Anions by Molecular Dynamics Simulations

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Quantum chemical calculations on phosphate/water systems, the development of potential functions and molecular dynamics simulations were performed in order to understand the interaction of the anions PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ with water molecules in clusters and solution. Geometry optimizations of the orthophosphate anion complex with water (PO_4^{3-}/H_2O) show that the most stable conformation has two symmetrical hydrogen bonds as part of a six-membered ring.

Analytical potential functions for the intermolecular phosphate-water pair interactions and an intramolecular force field containing anharmonic terms for phosphate anion were derived from ab-initio calculations and used in subsequent molecular dynamics simulations of aqueous solutions of potassium phosphate. The features of radial and angular probability distributions as well as other structural and dynamical data of the anions are derived from the molecular dynamics trajectories and compared with each other.

Molecular Dynamics Simulation of Liquid Formamide and N,N-Dimetylformamide with New Ab-initio Potential.

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Formamide (FA), N-methylformamide (NMF) and N,N-dimethylformamide (DMF) are interesting to physical chemists because they represent a transition from a hydrogen-bonded solvent without hydrophobic groups (FA) to an aprotic solvent with two hydrophobic methyl groups but still good electrolyte-dissolving properties (DMF). Moreover, knowledge of structural details of aqueous solutions of FA, NMF and DMF can provide substantial information about the interaction of water with protein chains, because one of the most important functional groups found in proteins is the peptide linkage -CO-NH, and understanding of the structure of hydrated peptide bonds is thus of considerable interest in structural biochemistry. In a previous paper we have reported results of a molecular dynamics (MD) simulations of pure liquid FA [1], aqueous solutions of FA [2, 3], and electrolyte solutions in water – FA mixtures [4, 5]. Present work extends these studies to liquid pure DMF.

The FA-FA and DMF-DMF potential functions were constructed based on *ab initio* calculations. The SCF interaction energies of molecular pair were obtained using the 6-311G** basis set of the Gaussian 98 program. The calculated set of approximately 6000 SCF energy points was then fitted to an analytical potential function of the atomic coordinates. One adjustable parameter was determined from agreement of the potential energy obtained from MD simulation with experimental data.

The MD simulations of pure components were carried out starting from random initial positions, orientations and velocities of molecules. Box side lengths corresponded to the experimental densities of FA and DMF, respectively. Then the systems were equilibrated for 200 ps. The temperature was kept constant by coupling to an external heat bath. The duration of subsequent runs was 200 ps for data collection. Spherical cutoffs were used to truncate intermolecular interactions at the distance of half box length. Shifted force modification of potential was employed to avoid truncation errors. The effect of a reaction field outside the cutoff on the electrostatic interactions was modelled by a Kirkwood approximation with the experimental dielectric constant values for liquid FA and DMF. The internal geometry of the formamide molecules was kept planar and thus the Newton equations of motion were solved using the general algorithm of the constraint dynamics.

Structural properties of the electrolyte solutions were investigated using the atom-atom radial distribution functions (RDF), dipole-dipole correlation finction and statistical geometry approach. The liquid structure properties are discussed in terms of a three-dimensional irregular packing, such as Delaunay simplices. Autocorrelation functions (ACF) were applied to study the translational/reorientational diffusion and librational/vibrational molecular motion.

Molecular dynamics simulations of pure liquid FA and DMF using OPLS and new *ab initio* model shown that both intermolecular potential functions give a qualitatively similar structural picture. However, the translational and rotational motions of FA and DMF differ substantially for these models. The agreement of reorientational times, hindered rotation frequencies and other kinetic properties of FA and DMF with data obtained from far-IR, low frequencies Raman and NMR study is much better with new model results than with OPLS data.

Molecular dynamics simulations proved as very suitable tool to study the structure and molecular microdynamics in pure liquid FA and DMF. The use of a new *ab initio* ion-molecular potential gave a realistic microscopic picture of the intermolecular motions and struture.

This research was supported by the Russian Foundation for Basic Research (grants No. 00-03-32973a and 99-03-32064).

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Mass Spectrometric Analysis of Solvate Clustering Compared to X-ray Diffraction and Theoretical Results for Lithium Halide Solutions in Methanol

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The recently developed technique in mass spectrometry proved to be a useful and efficient tool for direct observation of molecular clustering in a series of solvents as water, methanol, acetonitrile and others, as well as in their mixtures. An electrospray mass spectrometer, which allows the separate determination of oppositely charged clusters and specially designed for electrolyte solutions [1], has been applied for solutions of lithium halides in methanol. The results were then compared to the average structure obtained by the solution X-ray diffraction method and the differences in clustering can be interpreted by quantum chemistry, thermodynamics and computer simulations both in the jet stream and in the liquid state.

Mass spectrometric analysis has been performed on solutions of LiF, LiCl, LiBr and LiI in methanol as a function of concentration from 10^{-3} to 10^{-1} mol dm^{-3}, with the exception of LiF, where only the minimum concentration could be observed. The large difference in solubility of the lithium halides in methanol is expected to lead to visible differences in solvation and ion pair formation, and consequently, in clustering.

Among positively charged clusters, the solvated lithium ion was observed in all solutions, with the general formula $Li^+(CH_3OH)_n$, where n=1, 2, 3, ... is the number of methanol molecules included in the solvate cluster. Only a slight difference could be observed in the solvation of lithium ion in solutions with different anions, with a highest intensity appearing in clusters involving 3 to 4 methanol molecules. The highest observable number of n was 6 or 7. If we accept that all these clusters are produced by a simple fragmentation of the liquid droplet, without any secondary recombination of the fragments, a clear conclusion is that the coordination number of Li^+ can be as high as 6 rather than 4 in the liquid, an often debated question in the diffraction literature. In fact, our X-ray diffraction measurements on highly concentrated solutions of LiCl in methanol resulted in a coordination number 4 around Li^+ ion [2] at 6 mol dm^{-3} concentration but for 3 mol dm^{-3} a value of 6 was found.

It is generally accepted that (contact) ion pair formation in alkali halide electrolyte solutions is less probable even at high concentrations. Surprisingly, mass spectrometry results in a large series of salt clusters of general formula $Li^+(LiX)_n(CH_3OH)_m$, with n and m=0,1,2,3 ... and X=F^-, Cl^-, Br^-, or I^-. The formation of not solvated $Li^+(LiX)$ type clusters is in contradiction with the assumption of non existence of ion pair in these solutions, especially because the concentrations of solutions studied by mass spectrometry were very small.

The most intensive salt cluster formation with no or small amount of methanol was observed in LiCl solutions, while in LiI solutions salt clusters with n up to 4 and m up to 8 or 9 could also be observed. This enhancement in solvated clusters can be an effect of anion, a phenomenon well correlated with the change in coordination number along the series as we concluded from solution X-ray experiments (6 for Cl^- and 8 to 9 for I^-). The negatively charged ion clustering supports the same conclusion. The differences in anion solvation and clustering can probably explain the mechanism and thus, the differences in the solubilities along the alkali halide series in methanol.

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Molecular Dynamics Simulations of Liquid Chloroform at 298 and 220 K Using a Fractional Charge Model: Comparison with Raman and Neutron Scattering Results

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We present MD simulations of liquid chloroform at 298 and 220 K based on a model of 256 molecules per box with five fractional charges per molecule, situated at the respective molecular nuclei, and Lennard-Jones potential constants taken from accepted and most recent literature references, the computations being performed on a PC of 450 MHz using FORTRAN program code of the Daresbury Laboratory, UK. The agreement of the simulated and reported experimental Raman correlation functions of the reorientational motion of the symmetry axis of the molecules from a reported vibrational band deconvolution by a VV and VH polarization procedure, is near perfect at 298 K out to about 6 ps but only approximately good for the lowest temperature studied, 220 K. We also calculated the radial distribution functions for the carbon–carbon, chlorine–chlorine, hydrogen–hydrogen, carbon–chlorine, and hydrogen–chlorine separations but find only approximate agreement with previously published neutron scattering data at room temperature

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Ionic Dynamic in N,N-Dimetylformamide at Various Temperatures.

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The limiting ionic conductance in N,N-dimethylformamide (DMF) has been investigated using both conductance-measuring method and molecular dynamics (MD) simulations.

The conductances of MBr (M - Na^+, K^+, Cs^+, NH_4^+, Et_4N^+, Pr_4N^+, Ph_4P^+), $NaNO_3$, $NaBPh_4$, KI, $KClO_4$, Pr_4NBr, Bu_4NI, Bu_4NBPh_4, Ph_4PCl in DMF from 233.15 K to 318.15 K were measured. The data have been analysed by the Lee-Wheaton conductance equation in terms of the limiting molar conductance and association constant. Evaluation of single ionic conductance has been carried out using the Walden product of Bu_4N^+. The limiting ionic conductance coefficients (λ_o) and residual friction coefficient ($\Delta\zeta$) were analysed by means the continuum (Stokes, Zwanzing, Hubbard-Onsager) and molecular-continuum (Chen and Adelman) theories. All the experimental curves of the residual friction coefficient have minima. Similar dependences have been found for water, protic and aprotic organic solvents. The main contribution into thermodynamic properties comes from electrostatic ion-solvent interaction for small ions and from cavity formation for large ones such as tetraalkylammonium. The ionic radius increase leads to decrease of ion-solvent interaction and respectively to greater effects. Therefore the $\Delta\zeta$ decrease with the ionic radius increasing is caused by the electrostatic interaction decrease. Moreover cavity formation effect is greater for large ions.

MD simulations have been performed for Na^+, K^+, Cl^-, and Br^- in DMF in temperature range from 233.15 K to 318.15 K using a new *ab initio* intermolecular potential. Structural properties of the electrolyte solutions were investigated using the atom-atom and ion-atom radial distribution functions (RDF) and statistical geometry approach. Autocorrelation functions (ACF) were applied to study the translational/reorientational diffusion and librational/vibrational molecular motion in ion solvation shells. The dynamics of molecules in ion solvation shell was discussed in relation to structural properties and a self-consistent picture of intermolecular structure and motion has been obtained. Limiting ionic conductance coefficients calculated by means MD simulation λ_0^{MD} are in a good agreement with the experimental conductivity data λ_0^{exp} for Na^+, K^+, Cl^-, and Br^- ions in DMF

Ion	*T*, K	233,15	298,15	318,15
Na^+	λ_0^{MD}, cm/mol	11,78	27,27	38,35
	λ_0^{exp}, cm/mol	10,36	28,85	37,86
K^+	λ_0^{MD}, cm/mol	12,36	31,85	34,94
	λ_0^{exp}, cm/mol	10,81	30,70	40,88
Cl^-	λ_0^{MD}, cm/mol	14,10	51,75	61,35
	λ_0^{exp}, cm/mol	14,53	53,71	62,13
Br^-	λ_0^{MD}, cm/mol	17,11	54,83	65,98
	λ_0^{exp}, cm/mol	15,28	54,31	66,47

This research was supported by the Russian Foundation for Basic Research (grant No. 00-03-32973a).

BINARY and TERNARY METAL COMPLEXES of CONGO RED with AMINOACIDS

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The varied bioligical activities of sulfonated compounds have made them potential pharmacuetical agents and considerable lead compounds for the development of new drugs. Recently , complexes of aminoacids with sulfonated azo dyes have been constituted. These aminoacids are the ones most important in the binding interactions between protein and sulfonated macromolecules because of their basic side chains.

In this work , binary complexes of the sulfonated azo dye Congo red and 2-amino-4-methylpentanoic acid (LOS) and α-aminoglutaric acid (GLU) with +1,+2,+3 and +4 valuable metals and their ternary complexes have been investigated. The stability constant of the binary and ternary complexes of Ce^{+4} , Y^{+3} , Ni^{+2} , Co^{+2} and Ag^{+} with congo red as a primary ligand and LOS and GLU as secondary ligands have been determined from potentiometric titrations 25°C and 15°C at $I = 0.10$ mol/L $NaClO_4$. The thermodynamic parameters ΔG^o , ΔH^o and ΔS^o have been reported for the complexes formation reactions.

Cations in mixed water/acetonitrile solutions from MD simulations

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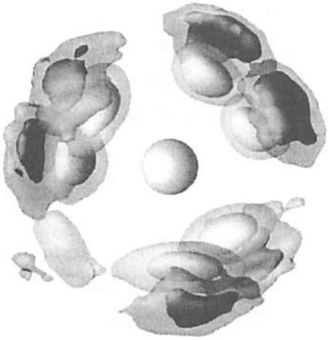
Abstract

We have performed Molecular Dynamics simulations in the NVT ensemble at room temperature for alkali and alkaline earth metal ions in 0%, 10%, 50%, 90% and 100% mixtures of water and acetonitrile. Water-water interactions were described by the SPC model, acetonitrile-acetonitrile interactions by Böhm's six-site model and cross solvent interactions by Lorenz-Berthelot combination rules.

Ab initio calculations at the MP2/TZP level including diffuse basis functions were performed to obtain both pure and effective ion-solvent pair potentials. The effect of the average many body effects has been studied.

The preferential solvation and coordination number has been determined. The average structure has been evaluated by means of spatial distribution functions.

For the ions with relatively fast exchange rate, the mean residence time and exchange mechanism will also be presented.



LARGE-ANGLE X-RAY SCATTERING, SMALL-ANGLE NEUTRON SCATTERING, AND NMR RELAXATION STUDIES ON CYCLOETHER-WATER BINARY MIXTURES

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At ambient condition 1,4-dioxane (*p*dio), 1,3-dioxane (*m*dio), and tetrahydrofuran (THF) are miscible with water at any ratio. By using various methods, such as infrared spectroscopy,[1] dielectric relaxation,[2] and ^{2}H-NMR relaxation,[3] many authors have investigated how the cycloethers are mixed with water. However, the structure of cycloether-water mixtures at the microscopic level has not been investigated directly by X-ray and neutron scattering techniques.

In the present investigation, we performed large-angle X-ray scattering (LAXS) and small-angle neutron scattering (SANS) measurements on *p*dio-water, *m*dio-water, and THF-water mixtures in a whole range of cycloether mole fraction, $0.0 \leq x_C \leq 1.0$ (C = *p*dio, *m*dio, and THF) to clarify the structure of the mixtures at the molecular level. The LAXS method gives us information on structure of the mixtures in a microscopic range of 0.1 – 20 Å, while the SANS method enables us to observe aggregates formed in the mixtures in a mesoscopic range of 10 – 1,000 Å. In particular, SANS method is a powerful tool to observe water aggregates because aggregation of cycloethers can be contrasted with solvent water by using D_2O. Furthermore, ^{2}H-NMR relaxation experiments were made on the cycloether-D_2O mixtures to elucidate their mixing states from the dynamics of D_2O molecules in the mixtures. The present LAXS results suggested that the structural change of clusters with mole fraction is not significantly different among these mixtures at the microscopic scale; at $x_C \leq \sim 0.1$ the hydrogen bonded network of water remains in the mixtures, at $x_C \geq \sim 0.3$ the inherent structure of cycloethers gradually predominates, and at $0.15 \leq x_C \leq 0.2$ both structures of cycloether and water are disrupted. The SANS results showed that the concentration fluctuation of these mixtures gradually increases with decreasing x_C and reaches a maximum at $x_C \sim 0.3$ – 0.4, suggesting that microheterogeneity occurs at this mole fraction range. However, the microheterogeneity is more enhanced in the sequence THF-water > *m*dio-water >> *p*dio-water mixtures. In addition, the rotational motion of D_2O molecules is more restricted in this sequence. On the basis of the present results, the effects of the size of cycloether molecules and the position of oxygen atoms in the molecules on the mixing states of the mixtures are discussed from the microscopic to mesoscopic levels.

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Comprehensive Study of Mixed Micelles: Diffusion Coefficients, Aggregation Numbers, and Counter Ion Bindings

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Tracer (self) diffusion coefficients of ionic micelles decrease with increasing micelle concentration while mutual diffusion coefficients of ionic surfactants increase with increasing surfactant concentration. The increase can be interpreted in terms of electrostatic interactions between micelles, counter ions, and surfactant monomer ions. In the case of one-component ionic surfactant, the micellar charge and surfactant monomer concentration are controlled by the total surfactant concentration. In the case of mixed surfactants, however, we can control the micellar charge and the monomer ion concentration.1)

We present here results of tracer and mutual diffusion coefficients as determined by the Taylor dispersion method, aggregation numbers as determined from the fluorescence decays of pyrene monomers solubilized in micelles, and monomer and counter ion concentrations as determined by ion-selective electrodes. When long-chain ionic surfactants, octadecyltrimethylammonium chloride ($C_{18}TACl$) and sodium octadecanesulfonate ($C_{18}SO_3Na$) were solubilized into nonionic micelles of octaoxyethylene dodecyl ether ($C_{12}EO_8$), tracer diffusion coefficients decreased monotonically with increasing concentration of an ionic surfactant. In the case of hexaoxyethylene dodecyl ether ($C_{12}EO_6$), when the long-chain ionic surfactants were solubilized, tracer diffusion coefficients increased first and then decreased with increasing concentration of the ionic surfactants. This first increase can be interpreted as due to the decrease in the micellar aggregation number. Using a surfactant selective electrode, the free monomer concentrations of the $C_{18}TA^+$ ion was determined and was found to be less than 1 % of the total $C_{18}TA^+$ ion. Using chloride and sodium ion-selective electrodes, degrees of counter ion binding were determined. Mutual diffusion coefficients were calculated using these data as well as tracer diffusion coefficients of counter ions, and are compared with the observed values.

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Transport of Water and Counterions in Montmorillonite

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Clays, and especially Montmorillonites, are used to store various types of wastes including nuclear wastes.

The understanding of transport properties of water and heavy element ions in those media is then of fundamental importance.

We present here a first principles approach of those processes. Monte Carlo and Molecular Dynamics simulations allow for the understanding of the swelling and transport processes for an atomic model of clay, counterions and water.

From this description, a self-consistent mesoscopic Smoluchowski model is derived which gives the possibility of evaluating observable currents and volume changes.

Self-Consistent Equilibrium and Transport Properties in Continuum Solvent Models of Ionic Solutions

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The continuum solvent models of solutions present usually non-consistent features when they are used to predict practical thermodynamic and transport coefficients for electrolytes. For equilibrium properties, the way from MacMillan-Meyer to Lewis-Randall level of description has been presented previously. The present work concerns the problem of reference frames for transport coefficients and their relations to the equilibrium quantities. The particular case of mutual diffusion in ionic solutions is emphasized. The correct treatment of the reference systems allows for an excellent description of both transport and equilibrium properties of electrolytes with the same parameters, up to concentrations as large as 2M in water, exhibiting the self-consistency of the model and its good agreement with available experimental data.

Individual Solvation Numbers around first transition metal ions in *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide mixtures

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Aprotic donor solvents *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA), have similar physicochemical properties such as relative permittivity, ε, donor number, D_N, and acceptor number, A_N. We have so far investigated halogeno and pseudo-halogeno complex formation of first transition metal ions thermodynamically, however, complexation behavior depends strongly on the solvent. In fact, except Zn(II) ions, complex formation of first transition metal ions in DMA is strongly enhanced comparing with that in DMF, though their structures are kept unchanged. The enhancement is ascribed to steric hindrance of acetyl methyl group of solvated DMA molecules.[1] In order to shed more light on ***steric solvation effect***, we have developed a titration Raman spectrophotometry system and determined individual solvation numbers around first transition metal ions in wide range of DMF-DMA mixtures.[2]

Balky aprotic donor solvents such as *N*,*N*-dimethylpropionamide (DMPA) 1,1,3,3-tetramethylurea (TMU) and hexamethylphosphoric triamide (HMPA), on the other hand, show strong solvation steric effect. In their solutions, metal ions decrease their coordination number and associated with a significant geometry change and remarkable enhancement of complexation. In this presentation, we report Raman spectroscopic study on the individual solvation number around first transition metal ions in mixed solvents, DMF-DMA, DMF-DMPA and DMF-TMU mixtures and discuss more details of the ***steric solvation effect*** and the ***steric preferential solvation***.

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Viscoelastic Behavior and Small Angle Scattering

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Abstract

In this contribution it will be investigated whether the structure of concentrated shear-ordered dispersions as determined by small angle synchrotron x-ray or neutron scattering can be rationalized in terms of viscoelastic flow behavior. Although so far scattering experiments have contributed little to the understanding of rheological systems we are convinced that rheological investigations will profit considerably from a better knowledge of the micro-structure of the dispersions.

Sheared dispersions are usually ordered in layers. There are two micro-structures of interest:

(a) The structure in a layer
(b) the structure between the layers.

One interesting point of mesogenic systems is their viscoelastic nature. There is strong evidence that the structure in the layer (a) can be treated as crystal-like, whereas, the structure between the layers (b) seems to be fluid-like. With scattering experiments one is in the excellent position that two experiments exist, with which the two effects can be investigated separately: The crystal-like micro-structure (a) can be determined at perpendicular incidence. The fluid-like micro-structure (b) is given by the intensity along the Bragg rods. In particular this second micro-structure may change its character in time by aging.

Here we were mainly interested to see the interrelation between rheology and scattering experiments. For scattering experiments this is most obvious at perpendicular incidence .

Oxidising Species in Molten Carbonates: Their Generation, Identification and Reactions on Nickel Metal and Oxide

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A promising future source of electrical energy is the fuel cell. The most promising at this time, for which demonstration plants have been built, is the molten carbonate fuel cell (MCFC). Fuel and air react in molten carbonate and the electrochemical conversion process takes place at the electrodes of the fuel cell.

To date there have been only two attempts at determining the extent of chemically dissolved oxygen in molten carbonates, (measuring the amount liberated on cooling and by titrating quenched samples with a reducing agent: the errors inherent in these methods are up to 100%). We have developed a much more sensitive method, based on the amount of UO_2 powder oxidised to uranate, for which very accurate analyses are available. The concentration and form of the oxidising species is of considerable interest, and discussion. The major possibilities are peroxide, O_2^{2-}, and superoxide, O_2^-, and we have developed a procedure that can differentiate between them. Our results so far apply to the ternary eutectic carbonate, $(Li,Na,K)_2CO_3$ at 450 °C, in which superoxide predominates, but since the MCFC employs $(Li,K)_2CO_3$ eutectic at 650 °C we are expanding our work and will present our findings at the Conference.

The MCFC also uses nickel metal and nickel oxide-based electrodes. We have determined the criteria for maximising the oxidising power of molten carbonates, by addition of nitrate and peroxide. Such melts can be used as an accelerated test of the resistance of these electrodes to oxidation and dissolution, respectively, and our latest results will be presented.

Enthalpy of transfer of $-CH_2-$ between water and organic solvents or mixed aqueous organic solvent systems

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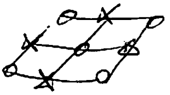
The $-CH_2-$ moiety is the basic building block of many hydrophobic molecules and of the hydrophobic parts of amphiphilic molecules. Thus understanding the solvation of $-CH_2-$ is central to understanding hydrophobic interactions.

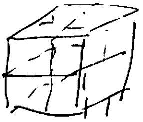
In the present paper we report the enthalpies of solution of n-alcohols, C_2H_5OH to $C_5H_{11}OH$ or $C_6H_{13}OH$, in water, a range of non-aqueous solvents and their aqueous mixtures These, and literature data for these solutes and for tetraalkylammonium halides in a range of non-aqueous solvents and in aqueous N,N-dimethylformamide solvent systems are used to calculate the average enthalpies of transfer of $-CH_2-$, $\Delta_t\overline{H}^\theta(CH_2)$, from the organic solvents to water and to the mixed aqueous solvents.

It is found that the $\Delta_t\overline{H}^\theta(CH_2)$ values between the organic solvents and water depend on the type of solute with those from the linear alcohls being close to zero.

In all cases $\Delta_t\overline{H}^\theta(CH_2)$ are positive into the mixed aqueous solvents, passing through maxima in the predominately aqueous solvent compositions. The magnitudes of the maxima vary with the organic component of the mixed solvent, as do the compositions at which the maxima occur.

3X3X1 3X3X3 3X3X5





Alkali Metal Chloride Clusters Showing Primary Step of Crystallization

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and
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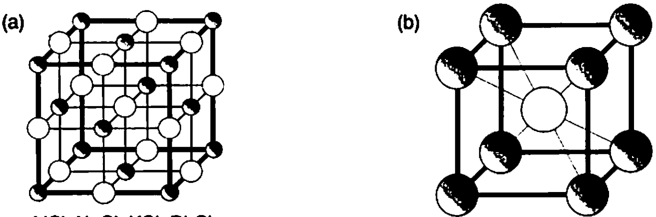
It is well known that the unit cell structures of alkali metal chlorides (LiCl, NaCl, KCl, RbCl, CsCl) in their crystals depend on their relative ionic radii. In case for LiCl, NaCl, KCl and RbCl where the radius of Cl^- is larger than that of the positive ion, a "NaCl-type" unit cell structure is present (Fig. 1-a); on the other hand, CsCl, in which the positive ion size is comparable to the negative ion's one has a different unit-cell structure called "CsCl-type" (Fig. 1-b). The electrospray mass spectrometry, which was specially designed for studying clusters generated from electrolyte solutions, gave the experimental evidence that the difference in the crystalline structures is originated from the clustering structure.

In the present experiments, clusters composed of alkali metal chlorides are formed in vacuum from their methanol solutions with concentrations $3 \times 10^{-3} \sim 2 \times 10^{-2}$ mol dm^{-3}, via vaporization of the methanol from the liquid droplets generated by the electrospray method. The resulting clusters were measured by an attached quadrupole mass spectrometer.

The alkali metal chloride clusters, $M^+(MCl)_n$: n = 0, 1, 2, 3···, where M^+ represents Li^+, Na^+, K^+, Rb^+ and Cs^+, were observed clearly. As for the NaCl-type crystal (LiCl, NaCl, KCl, RbCl), the clusters with n = 4, 13 and 22 which are in good agreement with the 3×3×1, 3×3×3 and 3×3×5 configurations, respectively, were observed in the form of prominent peaks. The 3×3×3 configuration agrees with the NaCl-type unit cell structure. On the other hand, the $Cs^+(CsCl)_n$ cluster did not show such a "magic-number" property. Furthermore, the mass distribution of the positive ion clusters ($K^+(KCl)_n$) was confirmed to be the same as that for the negative ion clusters ($Cl^-(KCl)_n$). This fact suggests the possible presence of electrostatic interaction between the positive and the negative ion clusters.

From these results, it will be discussed how the crystalline structure and the crystalline growth in the solution can be related to the cluster-level structure.



LiCl, NaCl, KCl, RbCl

CsCl

Fig.1 NaCl-type (a) and CsCl-type (b) unit cell structure.

THE THERMODYNAMIC BEHAVIOUR OF SOLUTIONS – IS A GENERALIZED APPROACH FEASIBLE?

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Given the diversity of solution types (electrolyte, non-electrolyte, polymer, self-organizing etc.) and their complex behaviour (phase transitions, solubility, critical behaviour) it may seem a hopeless task to pursue a generalized explanation for the thermodynamic behaviour of solutions. Indeed, in the decade 1949 – 1959 major treatises, still of relevance today, were given over to one only type of solution or solution behaviour.

The advent of computers and their application to solution behaviour in the mid – 1960s enabled greater access to insights from statistical thermodynamics which, at least to optimists, gave some hope that a generalized approach might be possible.

Thus, the pioneering work of Scott and van Konenburg demonstrated that the simple van der Waals equation of state for fluid mixtures was capable of qualitatively accounting for all of the complex P-V-T behaviour of such mixtures. Further, the theoretical work of Percus, Yevick, and Rushbrook enabled the cluster expansion approach of Mayer, initially applied to gases, to be directed at the thermodynamic behaviour of fluid mixtures and, again the advent of computers meant that such models such as Percus-Yevick and Hypernetted Chain could be tested for specific intermolecular potentials.

The success of this approach in explaining the P-V-T behaviour of simple fluids and the thermodynamic properties of mixtures of simple fluids influenced others such as Pitzer to successfully apply the same approach to the thermodynamic behaviour of simple electrolyte solutions. Since then, the pertubated hard sphere approach or mean spherical approach has been applied to a number of more complicated systems with a degree of success.

The vast majority of molecules are, of course, non-spherical and any generalized model would need to incorporate a size parameter. Some have devised ways of calculating a "hard-shape" potential, and compared the behaviour of solutions with related solvents in terms of the attractive remnant. Most recently a group have interpreted the dissociation constants of glycine in terms of this approach.

Equations such as that of van der Waals are based on mean field theories which have been shown to be deficient wherever fluctuations dominate the thermodynamic behaviour. Recent work by Prigogine on systems far away from equilibrium have given us a much clearer idea of the nature and role of fluctuations, as well as the underlying stability conditions for a system so affected. We now know that fluctuations are important at or near a critical point. We further know that algorithms associated with critical point indices are universal and appear to apply to phase transitions involving self organizing liquids. Thus some of the jigsaw pieces for a generalized approach to solutions appear to be available, and it may be worth pursuing the others to see whether a generalized approach is both feasible and useful in understanding their thermodynamic behaviour.

STRUCUTURE OF ETHANOL-WATER BINARY MIXTURES BY NEUTRON DIFFRACTION, EMPIRICAL POTENTIAL STRUCTURE REFINEMENT, SPHERICAL HARMONIC EXPANSION ANALYSIS

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Neutron diffraction measurements have been made at three ethanol mole fractions (0.1, 0.2, and 0.4) on 7 different isotopically substituted ethanol-water binary solutions, and using the isotopic substitution technique, the partial structure factors on HH, XH, and XX (X means all non-substituted atoms) were extracted on the ethyl-ethyl, hydroxyl-hydroxyl, and ethyl-hydroxyl pairs. Based on the neutron diffraction data, an empirical potential structure refinement has been performed to obtain all pair-correlation functions in the system, followed by spherical harmonic expansion analysis to calculate the orientational pair correlation functions. Discussion will be made on hydration of both hydrophobic ethyl group and hydroxyl one, aggregation of the ethyl groups, the size of hydrogen bonded clusters, orientational correlation between nearest neighbour molecules, and three-dimensional structure of the ethanol-water binary solutions with the three ethanol mole fractions.

An Application of Mass Spectrometry to Study of the Water Properties on the Cellulose Material Interface

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In this study, the thermodynamics characteristics of the water desorption process from cellulose material have been obtained by Knudsen's effusion method using mass spectrometer MI-1201.

The powder cellulose with polymerization degree of 700 and crystallization degree of 58 % has been used for experiment. The temperature dependence of the water saturated vapor pressures has been studied upon sample within humidity interval of 0.38-20 % and temperature interval of 278-303 K (Table.). The fixed volume of water evaporated out and was keeping inside of closed cell up to 20 hours in order to reach equilibrium during measurements of vapor pressures.

The dependence of water vaporous pressures (Pa) on temperature and humidity.

a, %	T, K			
	278	286	294	303
20,26	713,3	1286,9	2230,5	3866,0
16,02	533,7	1012,3	1919,8	3604,7
12,28	445,8	820,5	1480,2	2670,4
10,78	343,7	645,4	1199,9	2208,3
6,56	73,69	177,6	376,11	804,33
5,58	66,68	139,7	301,85	620,12
4,69	45,15	96,50	196,32	419,85
3,29	15,79	35,51	74,44	154,42
1,85	11,70	24,77	51,93	108,87
1,84	-	11,94	28,50	71,52
0,918	-	2,585	6,89	19,29
0,386	-	0,686	1,74	4,527

The pressure interval measured in cell during experiment was of 0.6-4000Pa. Therefore, the molecular effusion regime was keeping just for low humidity, while pressure didn't over 6 Pa. For more high pressure, the correction has been introduced, defined by transfer effusion regime, using pressure P, estimated from Hertz-Knudsen's equation. The correction is decreasing while the pressure is decreasing in accordance with dependence close to exponential curve. The equation for calculations of saturated vapors can be written as following:

$$P_{sat} = P\,[1,6-0,6\exp(-P/565)]$$

The enthalpy and entropy values of the water desorption on dry cellulose at temperature of 18 C has been obtained through extrapolation of enthalpy and entropy values to zero humidity and equal of $\Delta_{des}H=37,3\pm12,1$ kJ/mol and $\Delta_{des}S=59,1\pm19,2$ J/(mol K) respectively.

The estimated values of the water desorption characteristics from cellulose material are in good agreement with ones from the adsorption isotherm obtained. However, the method presented here allows to obtain reliable thermodynamic characteristics of studied process in region of low pressures.

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Poster Contributions

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Corrected Debye-Hückel Analysis of Surface Complexation

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ABSTRACT

Statistical mechanics in the framework of the Generalized van der Waals (GvdW) theory is used to clarify the mechanisms at work in surface complexation. A simple semi empirical theoretical framework is used for the derivation of the free energy of particle screening. Ion size effects are accounted for within a restricted primitive model of the electrolyte leading to a shift in the Debye screening length. This Corrected Debye-Hückel (CDH) theory was then used to calculate the bulk thermodynamic properties of electrolytes, such as the internal energy, the osmotic coefficient and mean ionic activity coefficients. Calculations and comparisons with the Monte Carlo simulations and to the experimental data have been performed for 1:1, 2:1, 3:1 and 2:2 salt solutions. A good agreement between the results of the CDH theory and simulations or experimental data was found for 1:1 and 2:1 electrolytes up to 1 M, whereas this agreement was less satisfactory for the cases of 2:2 and 3:1 electrolytes.

In order to describe the basic charging properties of colloidal particles in electrolyte solutions a simple theory of Charge Regulation (CR) has been defined. Short-range binding of potential determining ions to the particle surface is described by the concept of surface sites. In this work special attention is devoted to metal (hydr)oxide surfaces where the proton is considered as the potential determining ion. The CR theory allows for zero or single occupancy of the sites with a proton, which is characterized by a binding energy and a frequency describing the degree of confinement experienced by the proton at the site. A complete free energy expression, including both the long-range electrostatics and the short range binding of protons at the sites, was set up and minimized with respect to particle surface charge. By this method the surface charge as a function of pH was obtained for different sets of parameters. Results from comparisons with titrated experimental surface charge curves of metal (hydr)oxides at different electrolyte concentrations showed, as expected, that this simple model is not able to give a satisfactory description of experimental data.

Within the same framework an analysis of ion condensation and effective charge of the colloidal particles were therefore performed. This analysis defines a compact part (i.e. a Stern layer) of the screening and includes mechanisms as- i) nonlinear response to the electrostatic field, ii) ion-ion correlation effects of both electrostatic and steric origin. With this improvement the model results becomes much closer to the picture given by experimental data.

Theoretical Examination of Structure and Ion Solvation in Dioxane – Water Mixtures

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Interesting studies of ion solvation and - association especially of alkali halides in dioxane - water - mixtures are allowed, as the dielectric constant variies in dependence of the water content at room temperature from 2 to 80.

On molecular level some calculations were done, to study local equilibrium structures in these mixtures. Starting with quantum mechanical semiempirical and ab initio calculations of small molecule clusters, spatial pair correlation functions and thermodynamic characteristica were estimated with the help of integral equation methods (Site - Site - Ornstein - Zernike (SSOZ) equation) as well as with Monte Carlo simulations.

Especially interesting is the comparison of local solvation structures in these solvent mixtures with the solvation of alkali halides in nonaqueous polar fluids /1/, as well as a consideration of the influence of selective solvation on the structure of solvation shells.

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Enthalpies of Dilution of Aqueous Ionene Solutions

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

The enthalpies of dilution (ΔH_D, $c \rightarrow 0.002$ mol/dm^{-3}) of aqueous solutions of 3,3- 4,5- 6,6- and 6,9- ionenes with Br^- and Cl^- counterions, respectively, have been measured over a broad concentration range at 25°C. The enthalpies of dilution of 6,9- and 6,6-ionenes are exothermic in the low concentration range and become endothermic in more concentrated solutions. On the other hand the enthalpies of dilution of 4,5- and 3,3-ionenes are endothermic in the whole inspected concentration range.

The concentration dependence of the enthalpy of dilution of ionene solutions will be attempted to describe by a reasonable variation of different parameters of the classical polyelectrolyte theories.(2,3,4,5)

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SOLVATES AND SPECIFIC INTERACTION IN SOLUTIONS OF METHYL COMPOUNDS SUBGROUP OF ALUMINIUM

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This paper deals with solvates in solutions of binary systems of $Al(CH_3)_3$ - $In(CH_3)_3$, $Ga(CH_3)_3$ - $In(CH_3)_3$ with participation of pentacoordinated carbon atom in specific intermolecular interaction. Participation of pentacoodinated carbon is conditioned by the availability of essential non-divided $2s^2$-electron pair of carbon atom of element of methyl group of ligand [1]. On the basis of structural-energetic conformity and thermodynamic analysis of structural changes in solutions of binary systems of methyl compounds of aluminium's subgroup we discovered the existence of different structures of solvates with different specific intermolecular interactions of pentacoordinated carbon atom. We determined the dissociation energies of specific interaction of liquid components with different solvates of solutions of binary systems and the following rows of changing of the dissociation energy have been established:

Solvate I   Solvate II

$D_{In\text{-}CH3\rightarrow Al} < D_{Al\text{-}CH3\rightarrow In} < 4/5D_{Al\text{-}CH3\rightarrow Al}\,(8.26) < D_{In\text{-}CH3\rightarrow In}\,(8.42\ kD\cdot mol^{-1})$

Solvate I   Solvate II

$D_{In\text{-}CH3\rightarrow Ga}\,(6.30) < D_{Ga\text{-}CH3\rightarrow Ga}\,(6.55) < D_{Ga\text{-}CH3\rightarrow In}\,(7.80) < D_{In\text{-}CH3\rightarrow In}\,(8.42\ kD\cdot mol^{-1})$.

It is shown that energy of specific interactions in two different solvates with the same structure of isostructural components of system depends upon fulfilled rule of solvated molecules or solvated agent. The negative deflection an isotherm of vapour pressure from Raoult law have been established in that case when the energy of specific intermolecular interaction between molecules of components of solution is less then average value intermolecular interaction of molecules of two different components.

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QUANTITATIVE PARAMETERS OF THE COPPER(II) AND COBALT(II) CATIONS BEHAVIOUR IN AQUEOUS SOLUTIONS

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A great role of the hydrolytic reactions and in particular hydroxo polymerisation of metal ions in the electrolyte solutions determines an unremitting attention to this process. Investigation of the interaction of metal ions with solvents (water in our particular case) and also the finding out of the complicated relationship between chemical nature of ions and their behaviour in solutions have a special importance and also are the major tasks of the solution chemistry.

To obtain a number of important parameters of the Cu^{2+} and Co^{2+} cations behaviour in the single and binary component aqueous nitric solutions the group of physical and chemical methods of analysis was used. Basic pH ranges of the existence of mono- and polynuclear hydroxo complexes have been established, the hydrolysis constants for different temperatures, which were the basis for the determination of the thermodynamic values of the studying process (ΔH^{o}_{298}, ΔS^{o}_{298}) have been obtained. Kinetics of polynuclear hydrolysis of mentioned solutions have been studied and the rate constants, the Arrenius multipliers and the activation energies (E_a) have been obtained. The presence of two minimums on the E_a=f($[OH^-]/[M^{n+}]$) dependence for the solutions with the common existence of copper(II) and cobalt(II) ions was found out, it testifies the formation of stable heteronuclear structures (E_a are considerable lower in binary solution, than in individual ones). It substantiates the availability of the heteropolynuclear hydrolysis in this system and its mechanism has been proposed.

On the basis of obtained experimental data the stability constants of various complex species have been calculated and the diagram of distribution of different cationic forms in dependence on pH and $[OH^-]/[M^{n+}]$ with the consideration of the polynuclear hydroxo complex formation have been established. In this case hydrolysis begins under the lower pH-values and occurs within narrower range compared to the ideal solutions. The entire available experimental data on the behaviour of studied metal ions in the electrolyte solution and also the thermodynamic and kinetic parameters allow find out predominant role of the aqueous forms of metal ions and lead to conclusion that the mononuclear hydrolysis model is useless for the describing of occurring processes in the aqueous solutions with the cation concentrations more then 10^{-3} mol/litre.

METAL SOLVO COMPLEXES – MIXED HYDROXIDES – FERRITES

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One of methods of reception of ferrite with the given magnetic and electrical properties is the collateral precipitation of hydroxides of iron(III) and metal(II) with the subsequent thermal decomposition of them up to complex oxides. The advantage of the given method is a possibility to receive highly homogeneous mixtures without crushing and mixing of oxides. This method also allows to ensure high reproducibility of the physical, chemical and structural characteristics. As the structure of hydroxides is connected to a structure of hydroxo complexes in solution to predict result of collateral precipitation is possible on the basis of study of water solutions at various pH, [OH]/[M] meanings and ratio of ions of hydrolyzed metals.

In this connection on the basis of the curves of potentiometric titration the state diagrams of Fe(III)-M(II) (where M(II) = Co(II), Ni(II), Cu(II), Zn(II)) aqua solutions were obtained at common concentration of metal ions of 0.01 mol/l, representing dependence of pH and [OH]/[M], appropriate to equivalence points on the curves of potentiometric titration from composition of solution. On the basis of obtained diagrams and results of kinetic study, the thermodynamic and kinetic parameters of polynuclear hydrolysis of metals in Fe(III)-M(II) aqua solutions are established. The hydrolysis constants and activation energies of processes of polynuclear hydroxo complex formation are obtained. It is proved that the dominant influence on formation of hydroxo complexes in the investigated systems renders hydrolysis of iron(III). Solid phases of mixed oxides were obtained by thermal decomposition of corresponding hydroxides, and composition-structure relationships are presented.

Abstract of the poster presentation in the „Molecular liquids" session

Acetic anhydride as solvent or additive in analytical chemistry

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Acetic anhydride (Ac_2O)is a less pleasant solvent than acetic acid (AcOH), still its use as a solvent (alone or in solvent mixtures) is highly preferred nowadays in nonaqueous acid-base titrations. First of all pharmaceutical analyses (see e.g. *European Pharmacopoeia 2000*) use Ac_2O since it promotes the determination of very weak bases (and their derivatives). This promoting (or hindering) effect can be explained in part by acetylation. On the other hand, the Ac_2O molecules are known to have no proton donating (*i.e.* "acidic") abilities; on the contrary, they are able to accept protons. There are theories on the autodissociation of Ac_2O producing acetyl cation and acetate anion, but this equilibrium is repressed in the presence of acetic (or formic) acid. However, the presence of these solvent mixtures must be always considered since the titrant is perchloric acid in glacial acetic acid as usual. In the Ac_2O/AcOH system itself H-bonded interactions must be significant. The AcOH/Ac_2O/base and AcOH/Ac_2O/$HClO_4$ systems, existing and interacting with each other during the titration, are even more complex. We have tried to characterize and explain these equilibria by different experimental methods as well as by molecular dynamics calculations.

STRUCTURAL CHARACTERIZATION OF WATER/1-HEXANOL/$C_{12}E_{23}$ MICROEMULSIONS BY SMALL ANGLE X-RAY SCATTERING

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Microemulsions formed by water, 1-hexanol and dodecyle-poly(ethylene oxide-23) ether surfactant ($C_{12}E_{23}$, commercial name: Brij 35) have been investigated by small-angle X-ray scattering (SAXS) at 25°C. SAXS spectra were put on an absolute scale using water as a secondary standard [1].

The scattering data are evaluated using a well established indirect Fourier transformation method, ITP [2,3], to determine particle size and shape in real space. This method, however, is restricted to dilute systems with neglecting interparticle contributions to the measured scattering intensity. As some of the samples analyzed contain relatively high concentrations of dispersed structures, we also use the recently developed generalized indirect Fourier transformation method, GIFT [4,5], that enables a simultaneous determination of the scattering from the particles (form factor) and the interparticle correlations (structure factor) based on polydisperse hard spheres interactions.

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THERMO-PHYSICAL PROPERTIES OF DISACCHARIDE AQUEOUS SOLUTIONS

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To get some insight into the mechanisms of cryopreservation that characterize disaccharides, and to clarify the reasons that make trehalose the most effective bio-protector among disaccharides, we analyse the thermal properties of trehalose, maltose and sucrose aqueous solutions at different concentrations by using Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA). Calorimetric findings reveal a noticeable stronger trehalose-water interaction mechanism and a significant higher thermal stability in comparison with maltose and sucrose/water system. This can support the hypothesis of a greater effectiveness of trehalose in destroying the tetrahedral network of water compatible with the formation of ice. The effect of concentration on the water-disaccharide interaction strength has been also investigated.

VIBRATIONAL DYNAMICS IN HYDROGEN BONDED SYSTEM AQUEOUS SOLUTIONS

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Infrared spectra are obtained for trehalose water solutions at different concentrations from crystalline state up to 20 water molecules for each disaccharide molecule. Measurements were performed by using a Bomem DA8 Fourier Transform Infrared (FTIR) spectrometer in the 400-4000 cm^{-1}range. From the comparison of the spectra referring to different hydration with the ice spectrum, the effect of disaccharide on the structural arrangements and on the vibrational dynamics of water can be extracted. In particular, by observing the concentration dependence of the spectral features, it is found that the property of the bound water molecules changes from the ice-like water to liquid-like one.

ANALYSIS OF STRUCTURAL CHANGES OF WATER IN TREHALOSE AQUEOUS SOLUTIONS

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α,α-trehalose, a glass-forming disaccharide, shows an excellent bioprotective capability in several living beings under environment stress conditions, maintaining activity and leavening capacity of several desiccation-resistant organisms. In order to understand the reasons of this action, we have focused the attention on the molecular point of view. Experimental findings on aqueous solutions of homologous disaccharides (trehalose, maltose and sucrose) by Raman scattering support the hypothesis that the greater cryoprotective action of trehalose on biological structures is to be connected with its greater destructuring effect on the tetrahedral H-bond network of water, reducing the amount of freezable water. Neutron diffraction data, collected by using Sandals diffractometer at the ISIS facility (UK) indicates a decreasing of the tetrahedrality degree of water, by means of the changes of the characteristic peaks of the partial structure factors in comparison with water spectra and as a consequence of an increase of temperature.

RAMAN SCATTERING AND ACOUSTIC MEASUREMENTS ON POLYMERIC AQUEOUS SOLUTIONS

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We present low-frequency Raman scattering on Ethylene Glycol, EG, and Poly(Ethylene Glycol), PEG, of different molecular weights. The measurements were performed over a temperature range covering their respective glass transition temperature. The behaviour of the intensity of the boson peak can qualitatively be explained by changes in the number of enter-molecular degrees of freedom and by changes in the density of states. In order to study the hydration effect of EG and PEG and its dependence on the molecular weight, ultrasound velocity measurements on polymeric aqueous solutions were also performed.

Dependence of the molar conductivity of aqueous solutions of fullerenehexamalonates on temperature

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Electrical conductivity measurements on aqueous solutions of the sodium and calcium salts of fullerenehexamalonic acid, T_h-$C_{66}(COONa)_{12}$ and T_h-$C_{66}((COO)_2Ca)_6$, were carried out at four temperatures: 5, 15, 25, and 35°C, and in the concentration range from about 0.04 to 0.0001 mol COO^-/L. The limiting equivalent conductivities of the fullerenehexamalonate anion were estimated: Λ_0 [$^1/_{12}$ $C_{66}(COO^-)_{12}$] = 68.9, 91.4, 115.4, and 137.2 Ω^{-1} cm^2 mol^{-1}, respectively, at the temperatures of our measurements. Walden's product for the fullerenehexamalonate anion is practically independent of the temperature and is close to the theoretical value predicted by the Stokes' law.

Recent advances in the structural investigation of ionic solutions by means of X-ray absorption spectroscopy

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This presentation will focus on recent advances in the investigation of ionic solutions by means of the X-ray absorption fine structure (XAFS) technique. Over the last decade it has been shown that a new insight into the structural organization of ionic solutions can be gained by means of the XAFS spectroscopy. Novel structural information has been obtained due to the development of the theoretical framework for the interpretation of the XAFS in liquids and to the availability of low-noise experimental data.

The XAFS technique is especially well suited to provide accurate structural information on the nearest-neighbour coordination of ions in solutions. XAFS measurements can be made at very low concentration where the ion-ion interactions are negligible, thus providing the simplest experimental conditions for determining the solvent-ion interactions. This technique can be used to investigate the solvation structure of ions in organic solvents where the solubility is generally low.

The XAFS spectroscopy has been proven to provide reliable structural information on the ion-hydrogen pair distribution functions of ionic solutions, which can be very difficult or impossible to obtain by other experimental techniques. Moreover, recent studies have shown the ability of this technique in probing three-body correlation functions in ionic solutions.

A careful analysis of the K-edge XAFS data allowed us to achieve a conclusive description of the hydration structure of lanthanide(III) and 3-d transition metal ions in aqueous solutions. The presence of the hydrogen contribution and of three-body correlation functions has been detected, for the first time, in the experimental data. The solvation structure of these ions has been determined also in organic solvents, by means of the XAFS technique.

Models of Alcohol Mixtures: Supramolecular Ordering, Thermodynamic and Electrooptical Properties

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Generalized quasichemical models developed to describe a series of physicochemical properties of liquid mixtures opened up the possibilities in studying manifestations of supramolecular structure in thermodynamic, dielectric and optic properties [1,2].

Systems like acetone-alcohol and trichloromethane-alcohol present the mixtures of the polar associating substance in polar solvating solvent. Binary mixtures of acetone and trichloromethane with methanol and ethanol showing positive deviations from ideal solution behaviour contain a wide variety of supramolecular species due to hydrogen bonding between alcohol molecules and between acetone and alcohol, and trichloromethane and alcohol [3]. The structural model including chain-like infinite aggregation of alcohol, solvating by acetone or trichloromethane, and cyclic aggregation of alcohol have been developed to describe thermodynamic, dielectric, and optic properties of solutions.

Theoretical expressions are given for thermodynamic functions (activity coefficients of components, excess Gibbs energy, enthalpy and entropy), dielectric permittivity, dipole correlation factor, isotropic and anisotropic Rayleigh light scattering in the framework of unified quasichemical approach. The models of alcohol aggregates are coincided with the computer simulation of pure alcohols [4]. Thermodynamic properties and dielectric constant of binary mixtures were reproduced in the whole composition range and the wide intervals of temperature.

The thermodynamic parameters of chain-like and cyclic aggregation, e.g., equilibria constants, enthalpies and entropies of association and solvation as well as the structural parameters of aggregates have been obtained. The integral and differential parameters of aggregation were calculated.

The possibility is shown for the unified description of macroscopic properties of acetone-alcohol and trichloromethane-alcohol mixtures, and quantitative analysis of supramolecular ordering and molecular interactions by aggregation models.

Acknowledgements: This work was supported by the Russian Foundation on Basic Research (projects 00-15-97346 and 01-03-32051).

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INVESTIGATION OF SYSTEM PHOSPHORIC ACID – N,N-DIMETHYLFORMAMIDE AS POTENTIAL SOLVENT FOR CELLULOSE

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Aqueous solutions of phosphoric acid are the solvents for higher molecular cellulose. At present it is known that the interaction of this solvent with cellulose has a number of concentration peculiarities. It is established that there are three ranges of acid aqueous solution concentrations with different characters of interaction H_3PO_4 with cellulose. In particular, phosphoric acid with concentration more than 75% provides a maximum of cellulose dissolvation degree.

One of the possible mechanisms of the dissolvation process is connected with the presence in the solution of ions $H_4PO_4^+$ that are due to process of autoprotolysis. It can be supported that in non-aqueous solutions the autoprotolysis proceeds at less concentrations of phosphoric acid. In this way we carried out the investigation of the influence of organic solvent nature on the process of cellulose dissolvation in mixture H_3PO_4 – organic solvent. But to clarify the mechanism of cellulose dissolvation the knowledge of physical-chemical properties of solvent is necessary.

This report is devoted to the system phosphoric acid – N,N-dimethylformamide. The different physical-chemical properties such as specific conductivity, viscosity, density and solution enthalpies of H_3PO_4 in DMF were measured in the whole range of H_3PO_4 concentrations at temperatures 298-338 K.

It is found that the dissolvation of H_3PO_4 in N,N-dimethylformamide proceeds with essential exo-effects. On the basis of calorimetric experiment on solution enthalpies of sodium phosphate, hydrophosphate, dihydrophosphate and known solvation enthalpies ($\Delta_{solv}H^0$) of Na^+ the values of $\Delta_{solv}H^0$ for PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ were calculated.

The dissociation and autoprotolysis processes of orthophosphoric acid in N,N-dimethylformamide at different temperatures are discussed.

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

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Acetonitrile is the simplest and one of the most commercially important nitriles. It has achieved commercial importance in an increasing number of uses, e.g., solvent extraction, reaction media, organic chemical and an intermediate in the preparation of pharmaceutical. Moreover, its high dielectric constant and dipole moment make it an excellent solvent for polymers. The binary mixtures of acetonitrile with other liquid form mixtures which are cosolvent of polymeric materials. The liquid forming a cosolvent with acetonitrile can have different chemical structures. In this work we study the case of the amines.

In continuation to our investigation[1-2] involving volumetric properties of binary mixtures containing acetonitrile, in this work the density and excess molar volume of acetonitrile + (diethylamine or s-butylamine) have been determined as a function of composition at 288.15, 293.15, 298.15 and 303.15 K and under atmospheric pressure. Both systems exhibit negative excess molar volume values over the entire composition range. Results of measurements have been used to calculate excess partial molar volumes, partial molar volumes, apparent molar volumes and partial derivative molar volumes at infinite dilution of each component.

The partial derivative excess properties at infinite dilution appear to be interesting since at the limit of infinite dilution, the solute-solute interactions disappear. The values of infinite dilution excess partial molar volume provide information about solute-solvent interaction, independent of composition effect.

The results of the calculations will be discussed.

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CORRELATION AND MEASUREMENT OF MOLAR EXCESS GIBBS FREE ENERGY g^E AT 323.15 K AND MOLAR EXCESS ENTHALPY AT 298.15, 323.15 AND 343.15 K FOR WATER + 1,2-PROPANEDIOL, + 1,3-PROPANEDIOL, AND + 1,4-BUTANEDIOL.

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Molar excess Gibbs free energy g^E at 323.15 K and molar excess enthalpy h^E at 298.15, 323.15 and 343.15 K for binary solutions of water + 1,2-propanediol, + 1,3-propanediol, and + 1,4 butanediol have been determined over the whole composition range using a 601 Fischer recirculating ebuliometer and a modified 1455 Parr adiabatic calorimeter, respectively. All these systems exhibit positive values of g^E and negative values of h^E, the later turn less negative with increasing temperature. The obtained values of g^E and h^E for each systems have been correlated through the model proposed by Nagamachi and Francesconi[1] in which hydrophobic effects are included. Calculated values are in good agreement with the experimental values. A discussion about the influence of position of methyl group on alkanediol for hydrophobic hydration and the influence of the position of OH groups for hydrophilic hydration is also presented.

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PRESSURE EFFECTS ON THE SPIN-LATTICE RELAXATION RATES OF D NUCLEUS FOR D_2O MOLECULES IN ALKALI EARTH CHLORIDE AQUEOUS SOLUTIONS BY NMR SPECTROSCOPY

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The recent development in NMR has led to measure the spin-lattice relaxation rates (R_1) of D and ^{17}O nuclei of D_2O molecules in electrolyte aqueous solutions below 1.0 $molkg^{-1}$[1]. Since the structure of water is remarkably influenced by pressure, pressure effects on the rotational motion of the coordinated water molecules will lead to significant information on the dynamics of solvation. Therefore, we measured R_1 of D nucleus of D_2O molecules in alkali earth chloride ($MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$) aqueous solutions in the range of 0-1.0 $molkg^{-1}$ and 0.1-300 MPa at 25 ^0C. The spin-lattice relaxation times ($T_1=1/R_1$) were determined by the inversion-recovery (180^0-τ-90^0) pulse method on a JEOL GX-270 FT-NMR spectrometer. The R_1 values in these solutions decrease with increasing pressure and at each pressure is in this order : $MgCl_2>CaCl_2>SrCl_2>BaCl_2>D_2O$. They vary quadratically at 0.1-200 MPa and linearly at 250 and 300 MPa with concentration. The rotational correlation times (τ) for the D_2O molecules coordinated to Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} estimated by R_1 increase with increasing pressure. The τ is at each pressure in this order : $Mg^{2+}>Ca^{2+}>Sr^{2+}>Ba^{2+}>D_2O$.

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INVESTIGATIONS OF THE STRUCTURE OF CONCENTRATED AQUEOUS SOLUTIONS OF ALUMINIUM AND MAGNESIUM SALTS IN THE LIQUID AND GLASSY STATES

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Concentrated aqueous solutions of aluminium and of magnesium halides have been recently investigated by X-ray diffraction, under ambient conditions and in a glassy state (after their fast cooling into liquid nitrogen).

In the molecular models suggested to interpret the profiles of the diffracted intensities authors considered the existence of positional correlations between cation hydrates and between the cation hydrates and the anions beyond the direct contact. The adopted method was already used in previous investigations of the structure of these and of other aqueous solutions at room temperature [1-6].

Raman and inelastic neutron scattering spectroscopic investigations of the same solutions may be referred [7-9].

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Surface Complexation Models

Determination of the Inner Layer Capacitance from Surface Charge Curves

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ABSTRACT

To describe physiochemical processes at solid/liquid interfaces and interpret relevant experimental data surface complexation models have been successfully developed and widely used over the last decades. However, there are some problems in the application of these models if the number of adjustable parameters becomes too large, which is often the case in more sophisticated models. Previous studies have shown that quite often more than one parameter set can describe one set of experimental data equally well. To resolve these problems our research group is presently working with two different projects in parallel. In the first project the mechanisms at work in surface complexation are clarified by a theoretical reformulation using statistical mechanics. In the second project, which we shall focus on here, titrated surface charge curves are more systematically analysed by refocus on the Parson-Zobel approach developed decades ago. In that analysis the liquid part of the electrical double layer is divided into one inner layer and one diffuse layer part. The total capacitance C can then be expressed as two capacitors in series:

$$\frac{1}{C}=\frac{1}{C_i}+\frac{1}{SC_d},$$

where C_i is the inner layer capacitance, S the electrochemical surface area and C_d is the calculated diffuse layer capacitance. A plot of $1/C$ versus $1/C_d$ results in a straight line with a slope inversely proportional to S and an intercept providing the value for C_i. The electrochemical area obtained from this analysis can then be compared with the area measured using BET nitrogen adsorption technique.

In this work we have analysed own experimental data at different ionic strengths on goethite (α-FeOOH) and hematite (α-Fe_2O_3). The obtained values of S and C_i have been used as parameters in a 1-pK basic Stern surface complexation model. In addition, titrated surface charge data found in the literature for Fe_3O_4, TiO_2, ZrO_2 and RuO_2 have been analysed and modelled in the same way. The analyses and the model results show that some of these metal oxides behaves almost "ideal". The electrochemical area and the BET area are then very close and the model results almost perfectly fits the experimental data. On the other hand, the agreement for some other oxides is far from perfect. The electrochemical area sometimes becomes substantially higher than the BET area and the model can only give a poor description of experimental surface charge data.

In the light of these differences the following questions are discussed:

- What is a sound value of the inner layer capacitance of a metal oxide surface?
- Which site density is relevant to use in surface complexation modelling – a value found from titrations or from an estimation based on crystallographic information?
- What information can we get from measured zeta potentials?
- Is additional adsorption of electrolyte ions into the Stern plane necessary/relevant?

Hydration and Na^+-Binding in Aqueous Oxalate Solutions

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The interactions of the oxalate ion, $(COO)_2^{2-}$, with alkaline and alkaline-earth cations in aqueous solution, although weak, cause the toxicity of the anion and are important in a number of other fields. For instance, oxalate, which is formed by the decomposition of organic matter during the refining of bauxite via the Bayer process, creates significant problems in the recovery of the dissolved alumina from the sodium-rich concentrates.

We have used dielectric spectroscopy (DS) in the frequency range $0.2 \le \nu/\mathrm{GHz} \le 20$ to study the Na^+-binding and hydration of $(COO)_2^{2-}$ in aqueous sodium oxalate solutions up to the saturation limit, $c = 0.25$ mol/L, at 25°C. The complex permittivity spectra reveal a superposition of two dispersion steps which can be assigned to the co-operative relaxation of the hydrogen-bond network of bulk water and to the tumbling motion of sodium oxalate ion-pairs. Using literature information on Na^+ hydration, an effective hydration number of $Z_{IB} = 6.1\pm1.1$ was deduced for $(COO)_2^{2-}$ at $c \to 0$ from the concentration dependence of the solvent dispersion. From the relaxation time, τ_{IP}, and the relaxation strength, S_{IP}, of the solute relaxation, it can be inferred that doubly solvent-separated ion-pairs, $[Na^+_{hyd}((COO)_2^{2-})_{hyd}]^-$, are formed where both ions keep their hydration shell. For this complex, a value of the association constant $K_A^\circ = 11.0$ was obtained; its lifetime was estimated to be 1.0 ns. The rate of ion-pair formation, $k_{12} = 7.3\times10^9$ L/(mol·s), accessible from the concentration dependence of τ_{IP}, is about a factor of two smaller than expected for a diffusion-controlled reaction.

MD Studies of Intermolecular Vibrational Spectra for Isotopically Substituted Aqueous LiBr Solutions

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Molecular Dynamics (MD) simulations have been carried out for concentrated aqueous LiBr solutions, $(LiBr)_x(H_2O)_{1-x}$, x = 0, 0.05, 0.2, 0.15, 0.2, 0.25 and 0.33, in order to deduce intermolecular vibrational spectra $I_{ij}(\nu)$ (i, j = Li, Br, H and O) in the partial structure level.

The SPC/E potential[1] was employed to describe water-water interactions. As the pair potential between H_2O molecule and solute ion, the potential proposed by Koneshan al. was applied[2]. The internal vibrational motion within H_2O molecules was taken into account. MD simulations were performed using the MASPHYC program (FUITSU Ltd.) in the NTV ensemble at T = 298 K, with the systems which are constituted by 256 water molecules, and 0, 14, 28, 45, 64, 85 and 128 LiBr, respectively. The basic cell dimension was determined form the experimental number density for each solution. The time step was chosen to be 5×10^{-16} s. The simulation extended over 1.6×10^5 times steps after the equilibration, the initial configuration being random. The intermolecular "partial" vibrational spectrum was evaluated by the Fourier transform of the relative velocity autocorrelation function calculated for the i-j atom pair. Simulations for $(^{nat}LiBr)_x(H_2O)_{1-x}$, $(^{nat}LiBr)_x(D_2O)_{1-x}$, and $(^{6}LiBr)_x(H_2O)_{1-x}$ (nat: natural abundance) solutions were carried out in order to investigate the isotopic shift for the intermolecular vibrational bands especially $Li^+\cdots O$ and $Li^+\cdots Br^-$ ones, which have been observed in the isotropic Raman spectra.[3,4]

The $Li^+\cdots O$ vibrational spectra calculated for $^{nat}LiBr$-H_2O solutions exhibit well resolved peak at 160 - 200 cm^{-1} with an average D/H isotope shift of ca. -10 cm^{-1}, which is consistent with that observed from Raman scattering results. [3,4] The peak position of calculated $Li^+\cdots O$ band for 33 mol% $^{nat}LiBr$ solution (ν_{LiO} = 203 cm^{-1}) shifts toward lower-frequency side with decreasing LiBr content. This concentration dependence of the $Li^+\cdots O$ peak position agrees well with that reported from the Raman data.[3] The intensity of the intermolecular $O\cdots O$ vibrational peak at $\nu \simeq 60$ cm^{-1} found in 5 mol% LiBr solution drastically decreases with increasing LiBr content, which suggests that the cleavage of hydrogen-bonded network structure occurs in the concentrated LiBr solution.

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Concentration correlation function in liquid alkali-metal mutual solutions up to 1200K

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Statistical thermodynamics gives the possibility to determine the dispersion of the concentration fluctuation distribution as a long-wavelength limit of the concentration correlation function (the concentration-concentration fluctuation structure factor) $S_{cc}(0)$ in the form of

$$S_{cc}(0) = RT\left(\frac{\partial^2 \Delta G}{\partial x_i^2}\right)_{P,T}^{-1} = RT\left[\left(\frac{\partial \Delta \overline{G}_i}{\partial x_i}\right)_{P,T} \Big/ (1-x_i)\right]^{-1} = \left[\left(\frac{\partial \ln a_i}{\partial x_i}\right)_{P,T} \Big/ (1-x_i)\right]^{-1}$$

where ΔG, $\Delta \overline{G}_i$ - integral and partial Gibbs energies of formation, a_i - thermodynamic activity of component, x_i - mole concentration. Function $S_{cc}(0)$ when increasing defines an availability of concentration micro-inhomogeneties in solution, long range fluctuations and then a tendency to phase separation. Thus $S_{cc}(0)$ is a criterion of stability of the solution as a homogeneous one-phase system.

Since calculation of the function $S_{cc}(0)$ is connected with two differentiations of Gibbs energy of formation with respect to x_i, the $S_{cc}(0)$ is extremely sensitive to behaviour peculiarities of $\Delta G = f(x_i)$ and therefore to accuracy of its determining and approximating. Hence calculation of $S_{cc}(0)$ is an effective means for testing and coordinating both experimental data and theoretical models reproducing behaviour of the function $G = f(x_i)$.

In turn function $S_{cc}(0)$ is simply related to the long-wavelength limit of the structure factor $S(0)$ which is being defined in diffraction experiment with the small-angle scattering of X-rays and neutrons, i.e. the $S_{cc}(0)$ is structure-sensitive value. It may be obtained as a result of independent experiments (thermodynamic and diffraction) and thus be a showing of data inward agreement when the self-contained thermodynamic description of solution is building.

There are several works in literature fulfilled by the EMF, atomic absorption, X-ray and neutrons scattering methods where the function $S_{cc}(0)$ was plotted for some binary alkali metal systems. The temperature limit of these investigations was 673K.

The result of the submitted work is the construction of the concentration correlation function $S_{cc}(0)=f(T, x_i)$ for mutual metal solutions Cs-Na, K-Na, Cs-K at the temperatures up to 1200K in the concentration range $0 \le x_i \le 1$ on the base of our experimental data obtained in this area of state parameters. The study was founded on calorimetric measurement of the partial enthalpy of formation $\Delta \overline{H}_i$ in all the temperature interval and measurement of the partial Gibbs energy of formation by the effusion method at only one reference temperature 400K. These experimental data are input values for integration of the chemical thermodynamics differential equation $\left[\partial(\Delta \overline{G}_i/T)/\partial(1/T)\right]_{P,x_i} = \Delta \overline{H}_i$ being respectively integrand and boundary condition. Thus the algorithm of the research allows to determine Gibbs energy of formation at the high temperatures without resorting to its direct measurements in this area which would be extraordinary difficult with respect to alkali metals.

Behaviour pattern of function $S_{cc}(0)$ testifies to availability of ordering in the solutions under study as compared with random distribution in ideal solutions. Especially it displays for Cs-Na system which is characterized by the big size factor. The function $S_{cc}(0)$ for this system has rather narrow maximum in the concentration range $0{,}7<x_i<0{,}8$ demonstrating a presence of long range concentration fluctuations. This fact corresponds to behaviour feature of phase diagram: liquidus line is practically horizontal in this concentration range indicating the tendency to phase separation. The maximum is displacing to the center and the magnitude is decreasing with increase of temperature.

SOLUBILITIES IN THE TERNARY SYSTEM ELECTROLYTES-SUGARS-WATER

- SODIUM, POTASSIUM, GLUCOSE, GALACTOSE, XYLOSE -

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Most living organisms contain relatively high concentrations of ions, such as sodium and potassium. In spite of the similarity between these two ions, cellular distributions are different and asymmetric: the external concentration of sodium ions is higher than intracellular concentration and that of potassium ions is opposite. Such asymmetry, important to sustain various life processes, can be ascribed to their hydration properties, which might be reflected in the solubility of sugars in the electrolytes aqueous solutions. For elucidating the question of the dependence of solubility of sugars on the presence of electrolytes and also the effect of sugars on the solubility of electrolytes, it is of interest to study the solubility of some sugars in the presence of electrolytes, over a wide range of concentration. The literature describing the ternary system electrolytes-sugars-water is limited. The system sodium chloride-glucose-water[1] has been studied in a point view of its solid phase at 24 . The system potassium chloride-glucose-water[2] has been studied at 25. The present investigation was undertaken with the aim of providing more data of characterisation of the ternary electrolytes-sugars-water system and possibly to obtain a study of the solubility of sugars/electrolytes in the presence of electrolytes/sugars.

The determinations of sugars solubilities were carried out in NaCl aqueous solutions at 30. The solubility of xylose decreases linearly with increase NaCl concentration. The solubility curve of glucose is not simple, the solubility of glucose increases slightly during lower NaCl concentration and decreases gradually with increase NaCl concentration. The solubility of galactose increases linearly with increase NaCl concentration. Effect of NaCl on the solubilities of sugars depends on its concentration and kinds of sugars. NaCl have both actions, salting-in and salting-out. In case of KCl aqueous solutions at 30 the solubility of xylose increases linearly with increase KCl concentration. The solubility of glucose also increases linearly with increase KCl concentration, its slope is bigger than that of xylose. The solubility of galactose increases slightly with increase KCl concentration. KCl has only a salting-in action. The determinations of electrolytes solubilities were also carried out in the presence of sugars. In case of glucose the solubility curve of NaCl is not simple, the solubility of NaCl decreases with increase glucose concentration during lower glucose concentration and gradually increases with increase NaCl concentration. The curve of KCl is rather simple, the solubility of KCl is nearly constant during lower KCl concentration and gradually increases with increase KCl concentration.

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NEUTRON DIFFRACTION STUDY ON THE STRUCTURE OF CONCENTRATED AQUEOUS AMMONIUM CHLORIDE SOLUTIONS

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Hydration structure of ammonium ion (NH_4^+) has long been a matter of interest. Despite considerable effort to elucidating the hydration property of NH_4^+, the hydration number reported in the literature is widely spread from 4 to 11.[1] A neutron diffraction study with $^{14}N/^{15}N$ isotopically substituted 9.1 mol % $^*ND_4Cl$ in D_2O solutions has been carried out by Hewish and Neilson.[2] However, the number of water molecules in the first hydration shell of ND_4^+ was not determined unambiguously due to considerable overlap of the nearest neighbor N-O and N-D interactions in the observed distribution function, $G_N(r)$. Further neutron experiments employing a combination of $^{14}N/^{15}N$ and H/D isotopic substitutions are necessary to deduce partial distribution functions, $g_{NO}(r)$ and $g_{NH}(r)$.

In the present paper, we describe results of neutron diffraction measurements on five isotopically different aqueous 8 mol % $^*N^*H_4Cl$ solutions in order to obtain detailed structural information on the intermolecular hydrogen bonds between NH_4^+-H_2O and H_2O-H_2O within the solution.

Diffraction measurements were carried out using the ISSP 4G diffractometer installed at JRR-3M research reactor in Japan Atomic Energy Research Institute, Tokai, Japan. The incident neutron wavelength of $\lambda = 1.105 \pm 0.003$ Å was employed. Scattering intensities were collected over an angular range of $3 \leq 2\theta \leq 115°$, corresponding to $0.30 \leq Q \leq 9.69$ Å^{-1}. Observed scattering cross sections were combined to deduce partial structure factors, $a_{NO}(Q)$, $a_{NH}(Q)$, $a_{HH}(Q)$, $a_{XH}(Q)$ and $a_{XX}(Q)$ (X: O, N and Cl). Interatomic distances between NH_4^+ and the nearest neighbor H_2O molecules were determined to be $r_{NO} = 2.87(1)$ Å and $r_{NH} = 3.44(2)$ Å, from the least squares fitting analysis to the observed $a_{NO}(Q)$ and $a_{NH}(Q)$, respectively. The average number of H_2O molecules within the first hydration shell of the NH_4^+ was determined to be 3.9(1), implying the tetrahedral hydration geometry of NH_4^+. Structural parameters on intermolecular hydrogen bonds among H_2O molecules were determined to be $r_{HH} = 2.42(1)$ Å, $r_{OH} = 1.91(1)$ Å and $r_{OO} = 2.78(1)$Å, respectively.

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Supercooling of aqueous solutions of alcohols and sugars

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Studies of aqueous solutions at low temperatures are important in various fields including cryopreservation of living cells, climate physics and food preservation at low temperatures. Despite many studies, there have been few systematic studies as to how the nature of a solute affects the supercooling behavior of aqueous solution.

In this study, we have measured the homogeneous nucleation temperatures (T_H's) of aqueous solutions of various alcohols and sugars as a function of solute concentration. The alcohols used were methanol, ethylene glycol, glycerol and xylitol, and the sugars used were glucose, fructose, sucrose, maltose and trehalose. The emulsification method developed by Rasmussen and MacKenzie[1] was employed to measure T_H of these aqueous solutions. The dispersant phase was a 1:1 mixture of methylcyclopentane and methylcyclohexane. The surfactant used was Span 65 (sorbitan tristearate) which has been used in many emulsification works of aqueous solutions[2]. The cooling rate was about 10K/min in most cases.

The obtained T_H results clearly indicate that deep supercooling is observed for the solution of an alcohol (a sugar) having many OH groups. This trend is linked with the inhibition of ice nucleation by the OH groups which make hydrogen bonds with surrounding water molecules. All aqueous disaccharide solutions (disaccharide = sucrose, maltose and trehalose) give almost identical T_H values over whole sugar concentration ranges investigated, suggesting that the differences in molecular configurations exert little effect on the magnitude of T_H in aqueous sugar solution.

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ADSORPTION BEHAVIOUR OF STRONTIUM ON ROCK

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Mobility and transport of radionuclides in the geosphere are influenced by their interaction with solids. One of the main components of solid are rocks. Strontium is very hazardous nuclide because its high solubility makes it likely to migrate through graund water to the biosphere. This mobility can be considerably reduced by adsorption of strontium on the rocks and minerals surrounding the nuclear waste repository. The adsorption of strontium on rocks have been aimed at providing data that can ultimately be used to predict migration rates in the host rocks surrounding the storage site. In this study adsorption of strontium on rock was investigated by bath-type procedure and radiotracer technigue. The uptake and distribution coefficient (K_D) determined depending on mass of solid, solution volume and the ratio of volume of solution to that of mass of solid (V/m). An initial strontium concentration range of between 2.10^{-3}M to 2.10^{-4} M . Adsorption followed Freundlich type isotherm and linear adsorption isotherm was obtained for equilibrium concentrations. Adsorption data was fitted to the first order rate equation and k_1 , k_2 rate constants were calculated for rapid and slow adsorption processes.

HETEROPOLYNUCLEAR HYDROXO COMPLEXES OF CHROMIUM(III) WITH ALUMINIUM(III) AND SCANDIUM(III) IN WATER SOLUTIONS

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A problem of the polynuclear hydrolysis of metal ions as in the single-component and so in the water solutions containing several hydrolyzed metal ions is reviewed in the report on the basis of results of the study by the set of physicochemical methods. The kinetics, mechanism and optimal conditions of the heteronuclear hydroxo complex formation, thermodynamic stability of such solvo complexes, phase transfer of them into the composite hydroxide precipitate with conservation of the majority of the basic structural performances is considered.

The activation energies of polynuclear hydrolysis of metal ions are determined and the kinetic advantage of formation of heteronuclear fragments is proved. The dependence of an activation energy on a molar ratio $[OH^-]/[M^{3+}]$ is obtained and three basic areas of pH and $[OH^-]/[M^{3+}]$, corresponding to the beginning of hydrolysis, formation of the polynuclear hydroxo complexes and precipitation of the hydroxidic deposit are determined. The compensation effect between magnitudes of an activation energy and Arrenius factors confirms the made deductions about the multiphase mechanism of hydrolysis and testifies that the pH variation does not render noticeable influence on the integral rate of polymerization.

The diagrams of distribution of cationic hydroxo complexes in a wide pH and $[OH^-]/[M^{3+}]$ range are obtained in view of polynuclear hydrolysis and the areas of the prevalence of certain complexes are determined. The beefing-up of hydrolysis of ions Cr^{3+} in presence of the more labile hydroxo complexes of Al^{3+} and Sc^{3+} is justified at the expense of formation of the heteronuclear fragments which are not breaking up for a long time due to inert properties of aqua-hydroxo complexes of chromium(III). The thermodynamic parameters of the polynuclear hydrolysis in mixtures containing several hydrolyzed metal ions are obtained and their correlations with composition of solutions are determined. The influence of an electronic structure of metal ions on the quantitative arguments of formation and disintegration of polynuclear fragments is esteemed.

The all-up learning of the Cr(III)-Al(III) and Cr(III)-Sc(III) heteronuclear hydroxo complex formation of has allowed to determine optimal requirements for their transfer into a solid phase which appears to be a prestructure at deriving new hydroxidic and oxidic materials with molecular distribution of the components. The synthesis and learning of them by IR spectroscopy, differential thermography, X-ray phase and chemical analysis is held. The reliable correlations between composition, structure and properties of dissolved hydroxo complexes and receivable on their basis oxidic materials are retrieved.

ADSORPTION OF MITOXANTRONE ON GLASS POWDER

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The adsorption behaviour of Mitoxantrone (Mx) on the acid-treated and non-treated glass powder was compared. The adsorption experiments were performed by using batch method depending on time, concentration, particle size and temperature. The adsorbed amounts of Mx in equilibrium on acid-treated glass powder (GPa) were found to be much smaller than those found for non-treated glass powder (GPn). These results were correlated with structural properties of glass powder such as porosity, surface charge and surface area. These experiments were carried out in 3.10^{-5} – $1.2.10^{-3}$ M concentration range on glass powder with particle diameters $r<125$ and $125<r<250$ μm. The ratio of solution to the adsorbent was chosen 100 cm^3g^{-1}. Solution concentrations were determined spectrometrically. Conductivity and pH of initial and final solutions were checked and used for interpretation of adsorption results. The amount of adsorbed material is inversely proportional to the partical size. The adsorption data were fitted to B.E.T. and Freundlich isotherms. Adsorption capacities of GPa and GPn and adsorption equilibrium constants were calculated from isotherm data. On the acid-treated glass powder, as the temperature increased, was decreased amount of adsorbed and the enthalpy of reaction was found to be positive, ($\Delta H>0$). The experiments were repeated at the different temperatures and the amount of the adsorbed material as a function of 1/T are plotted. In the GPn a completely contradictory condition was observed, and the enthalpy of reaction was found to be negative, ($\Delta H<0$). By comparison of the adsorption heats and pH and conductivity values in equilibrium, the adsorption mechanism was elucidated.

ANALYSIS OF THE L-ASCORBIC ACID/WATER INTERACTION BY NEUTRON SCATTERING

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The reducing action of Vitamin C (L-ascorbic acid), strictly connected to its instability, is on the basis of its positive effects on human health. From the physical chemistry point of view, Vitamin C, due to both its relatively small dimension and to the existence of H-bond interaction sites, can be considered as a model-system for the study of solute-solvent interaction mechanisms. Since the literature on Vitamin C-water molecular H-bonded interactions is relatively poor, our purpose is to get information on molecular mechanisms regulating its biological functions, in which the hydrogen bonding plays a key role.

In this contribution we show neutron scattering findings on L-ascorbic acid aqueous solutions. By the characterization of the translational, rotational and vibrational contributions to the motion and the quantitative evaluation of important quantities (hydration radius, hydration number, mean-square displacement), we can estimate the strength of the L-ascorbic acid/water interaction and its influence on the diffusive dynamics of both L-ascorbic acid and water.

NEUTRON SCATTERING STUDY ON FRAGILE GLASS-FORMING AQUEOUS SOLUTIONS

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Neutron scattering measurements on trehalose/H_2O and sucrose/H_2O mixtures have been carried out by using the spectrometer MIBEMOL at the Laboratoire Leon Brillouin (LLB, Saclay). The investigated temperature range was 88 K- 283 K, through the glass transition temperature $T_g \cong 233$ K. The study is principally addressed to the comparison of the vibrational properties of the two homologous disaccharides across the glass transition. Through the temperature behaviour of the Debye-Waller factor, the different rigidity of both the disaccharide/H_2O mixture has been characterized. Finally, the dependence of fragility on concentration has been also investigated for the trehalose/water mixtures.

STUDY ON „FRAGILITY" OF VITAMIN C / WATER SYSTEM ACROSS GLASS TRANSITION

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Vitamin C (L-ascorbic acid) is involved in a great number of important biochemical reactions in the human body. Two of its major interactions are in aiding the synthesis of the protein collagen and potentiating the immune system. Recently it seems that an excessive dose of Vitamin C results to be harmful for human health, being linked to cell damage and increase of artherious thickness and may act as a prooxidant causing damage to DNA.

In this paper the results of neutron scattering measurements, performed on Vitamin C/H_2O mixtures as a function of temperature by using the spectrometer MIBEMOL (LLB, Saclay), are reported. They furnish qualitative and quantitative information on the relative importance of the relaxational and vibrational contributions of the Vitamin C/water system spectra. By the evaluation of R_1 parameter, connected with the fragility of the system, the Vitamin C/water system has been collocated as an *intermediate* system in the Angell scheme.

STUDY OF HYDROGEN BONDED SYSTEMS COORDINATION BY VISCOSITY AND ULTRASONIC VELOCITY MEASUREMENTS

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We report viscosity and compressibility measurements on trehalose, maltose, and sucrose aqueous solutions at different concentration and temperature values. What emerges is that trehalose shows, in comparison with maltose and sucrose, a higher interaction strength with water which gives rise to a greater value of hydration number in all the investigated temperature range. Furthermore, viscosity measurement reveal that trehalose, at high concentration, values shows in respect to the other disaccharides, a "stronger" kinetic character namely a lower structural sensitivity to temperature changes in the investigated temperature range. This result could explain the greater cryptobiotic attitude of trehalose at high concentration.

The Influence of Initial Parameters on Metal Content in Equilibrated Organic Phase at Extraction with Phosphoric Extractant

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Within the scope of investigation of extraction and separation of cobalt(II) and nickel(II) with commercial organophosphorus extractants and as an extension of earlier investigations of factors influencing extraction in such systems the influence of the initial concentration of extractant [0.5 - 20 % (v/v)] and the initial phase volume ratio (organic to aqueous) [0.5 and 1] on metal content in the organic phase and in this connection on the relationship between initial pH and pH in equilibrium was studied.

Samples were prepared with metal a content [0.15 g/L Co and 2.3 g/L Ni] corresponding to that obtained by leaching some real materials (e.g. lateritic ore from locality Kosovo) with sulphuric acid. Samples containing single metals or their mixture in sulphate solution were treated, at initial pH = 8 and 25± 0.1 °C, with the phosphonic extractant mono-(2-ethylhexyl)phosphonic acid (2-ethylhexyl) ester [MOOP] and the thiophosphinic extractant bis(2,4,4-trimethylpentyl) monothiophosphinic acid [Cyanex 302] using kerosene as diluent.

Decrease in pH in equilibrium for constant initial pH differed as a result of the stoichiometry of extraction reaction of given metal, extractant and diluent as well as a result of a combined influence of initial concentrations of metal and extractant, and the initial phase volume ratio.

The influence of the initial concentration of extractant on metal content in the organic phase differed. Generally, it was much stronger for the initial phase volume ratio 0.5 than for 1, and in the case of extraction with MOOP than in extraction with Cyanex 302. Changes in metal content were also more pronounced for nickel than for cobalt. Only in the case of Cyanex 302 (for both initial phase volume ratios) the content of cobalt in the organic phase changed only slightly with a change in the initial concentration of extractant.

Highest contents of cobalt in the organic phase were obtained with Cyanex 302 and the initial phase volume ratio 0.5 in the presence of nickel. Highest nickel concentrations were achieved with MOOP and the initial phase volume ratio 0.5 but in the absence of cobalt. This was result of a mutual action of cobalt and nickel which was observed for both extractants and was stronger in the case of theinitial phase ratio 0.5 .

THERMOCHEMISTRY OF THE LIQUID-PHASE IODIDE–THREE-IODIDE ENVIRONMENTALLY SAFE REDOX-PROCESS OF PROCESSING OF HYDROGEN SULPHIDE-CONTAINING GASES

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The research of thermodynamics of the reactions of liquid-phase processes of the processing hydrogen sulphide-containing gases introduces an important problem at creation of the wasteless or low-waste technology in many fields of industry. The pure technology should ensure not only indispensable degree of clearing gases from hydrogen sulphide, possibility of obtaining a commodity output from H_2S, but also to not permit pollution of the environment by it and other rather toxic sulphuretted compounds.[1-4]

In the given activity the liquid-phase iodide–three-iodide redox-process, based on usage of the following reactions (with regeneration of oxidant by chemical or electrochemical methods) was studied:

$$H_2S_{\text{gas}} + H[I_3]_{\text{aq}} = S_{\text{rhomb}} + 3\ HI_{\text{aq}}; \qquad (1)$$

$$3\ HI_{\text{aq}} + 0{,}5\ O_{2\ \text{gas}} = H[I_3]_{\text{aq}} + H_2O_{\text{aq}}; \qquad (2)$$

$$2\ H^+ + 2\ e^- = H_{2\ \text{gas}} \quad \text{(process on the cathode);} \qquad (3)$$

$$2\ H^+ + 2\ e^- = H_{2\ \text{gas}} \quad \text{(process on the anode).} \qquad (4)$$

In connection with that the direct research of the reaction (1) is integrated to known methodical and technical difficulties, in isoperibolic calorimeter of dissolution the values of enthalpies of the reactions of interaction of three-hydrate of sodium sulphide with solution of iodine in iodic acid and with solution of iodic acid were measured.[5] By combination of these reactions with the reaction $H_2S_{(\text{HI; aq})} \rightarrow H_2S_{\text{gas}}$ the thermochemical equation of the investigated iodide–three-iodide process was obtained. On its basis with the usage of reference data on enthalpy and entropy of the substances taking part in the reactions of drawn up thermochemical cycle missing in the literature relation of enthalpy of dissolution of gaseous hydrogen sulphide in iodic acid from the concentration of ions hydrogen, the value of enthalpy of the reaction (1) which has interest for us and also temperature relations of Gibbs energy ($J \cdot mol^{-1}$) and the equilibrium constants of this reaction were obtained:

$$\Delta G^{\circ}_T = (-92400 \pm 5200) + (79 \pm 3{,}1)\,T; \qquad \ln K_c = [(11114 \pm 626)/T] - (9{,}5 \pm 0{,}4).$$

The possibility of the usage iodide–three-iodide of process both with the thermodynamical and technological points of view is shown. Thus, the precipitation reaction of sulfur by solution of the iodine complex even at 373 K remains practically irreversible. And the regeneration of the waste solution by chemical or electrochemical methods which do not influence on environment negative impact is possible.

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Coordination Chemistry of the Copper(I), Silver(I) and Gold(I) Ions in Phosphites, Phosphines, Liquid and Aqueous Ammonia. A Vibrational, EXAFS and ^{63}Cu NMR Spectroscopic Study.

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The coordination chemistry of the ammine solvate complexes of copper(I) and silver(I) in liquid and aqueous ammonia has been studied by means of vibrational spectroscopy. Previously reported data have shown that the symmetric metal-ligand stretching frequencies are observed at 370 cm^{-1} for linear $Ag(NH_3)_2^+$ and 290 cm^{-1} for tetrahedral $Ag(NH_3)_4^+$ formed in aqueous and liquid ammonia, respectively.[1] Copper(I) and silver(I) ions in aqueous ammonia are linear with Cu-N and Ag-N bond distances of 1.88 and 2.22 Å, respectively.[2,3] Recently recorded Raman spectra show a weak metal-ligand stretching vibration at 320 cm^{-1}, indicating a coordination number of four copper(I) in liquid ammonia. ^{63}Cu NMR measurements on the ammine solvated copper(I) ion in aqueous and liquid ammonia are in progress.

Coordination chemistry changes have been observed when the soft monovalent d^{10} metal ions are transferred from oxygen or nitrogen to sulfur donor solvents.[4] These ions are all tetrahedral in the oxygen and nitrogen donor solvents,[5] while in the sulfur donor solvent *N,N*-dimethylthioformamide, D_S = 52,[6] the copper(I) and silver(I) ions have tetrahedral, and the gold(I) ion has linear configuration.[4] Phosphorus donor solvents are regarded to have even softer bonding character; the D_S values of tributyl phosphite and tributyl phosphine are 56 and 76, respectively.[6] The structures of the triethyl phosphite and tri-n-butyl phosphine solvates of the copper(I), silver(I) and gold(I) ions will be presented, and the cause of different coordination numbers will be discussed.

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ION ASSOCIATION of HEXAMMINE COBALT COMPLEXES in ETHANOL-WATER MIXED SOLVENTS

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In the previous studies, the ion association of hexammine cobalt (III) with various anions had been investigated extensively in aqueous solutions by conductometric methods. It seemed interesting to study the association equilibrium of these unsymmetrical complex sats in water –organic solvents systems.Thus, conductance measurements of the complex salts in ethanol-water mixed solvents were undertaken for purpose of the studying the change in ion association equilibrium with the variation of the composition of the solvent mixture.Our aim in the present study, is to investigate interaction of solvent and temperature on interaction with monovalent anions of cobalt (III) complexes.In these study, first the electric conductivities of 10-80 % ethanol-water mixed solvents of the chloride , bromide , iodide , nitrate and perchlorate of hexammine cobalt (III) are measured at nine temperatures between 10 and 50 ^{0}C. The ion association constants (K_A) have been estimated by analyzing conductivity data in terms of the Robinson-Stokes equations. The Robinson-Stokes equations are used here to provide a better fit to the data of unsymmetrical electrolytes.It has been found that the molar conductivities of these salts in 10-80 mole % ethanol-water mixed solvents, in general, increased in the order chloride < bromide <nitrate<iodide < perchlorate. This behaviour of complex salts may be dependent on increasing of the limiting ionic conductivities of anions in medium of the solvent. The limiting ionic conductivities of the bromide, iodide, nitrate and perchlorate ions in 10-80 mole % ethanol-water mixed solvents at nine temperatures has been calculated by Kohlraush equation.It has been observed that the order in magnitude association constants among the complex salts is chloride < iodide < bromide < perchlorate < nitrate and this order is dependent on the temperature and the percentage of the composition of the solvent mixtures.Besides, the association constants are increased with a decrease in the d electric constant of the solvent.This result is in good agreement with many paper. The thermodynamic parameters have been calculated from the ion association constants by using Van't Hoff equation.These constants were compared each other.

Thermodynamics of Aqueous Solutions of Some Lower Poly(ethylene glycol)s

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Abstract

The osmotic coefficients of aqueous solutions of ethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (TTEG) were determined by freezing point measurements. On the basis of these data the activity coefficient of the solute, the excess Gibbs energies of solution as well as the respective partial molar functions of solute and solvent were determined. The difference in the Gibbs free energy of solvation for the solvent in solution relative to the pure solvent was calculated and the limiting effect of a solute on the solvation thermodynamics of a water molecule was shown. From these results it may be concluded that these systems behave rather non-ideally and that the solvation process as well as the structural changes of the solvent depend primarily on the molecular weight of the solute molecule.

Prediction of Water Activity in Aqueous Salt-Polymer Systems Using Polymer Scaling Laws

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Water soluble polymers have been utilized very extensively in many different industries like petroleum, paint, adhesives, pharmaceutics and so on. Recently, these polymers are also employed in biotechnology for large scale biochemical extraction[1, 2]. These industries require knowledge of numerous physical property data for any process design calculations. Accordingly, thermodynamic properties such as activity or chemical potential in polymer-salt-water system is needed to perform phase equilibrium calculations for extraction equipment design.

In this work a model which is based on the solution theory of Hill and Hill was used. In this model the effect of polymer molecular mass is concerned by means of polymer scaling laws. Using the solution theory of Hill, the chemical potential of water in the salt-polymer-water system is as follows:

$$\frac{\mu_w - \mu^{\circ}_w}{RT} = v_s m_s + v_s \int m_s \frac{\partial \ln \gamma_\pm^{LR}}{\partial m_s} dm_s + m_p + v_s^2 C_{ss} m_s^2 + C_{pp} m_p^2 + v_s^3 C_{sss} m_s^3$$

$$+ C_{ppp} m_p^3 + 2v_s C_{ps} m_p m_s + 3v_s C_{pps} m_p^2 m_s + 3v_s^3 C_{pss} m_p m_s^2 + \cdots$$

which water activity a_w can be related to chemical potential:

$\mu_w - \mu_w = RT\ln a_w$

In the eqn. 1 $\gamma_\pm^{LR}$ is salt activity coefficient, and C_{ss} and C_{sss} are Hill osmotic virial coefficients for electrolyte solution. The values for C_{pp}, C_{ppp} and C_{ps} can be obtained by scaling laws. For example the scaling law for C_{pp} is as follows:

$C_{pp} = d_w(b_{pp}N^{3v} - NV_{MP}^{\infty})$

Where d_w is the density of water, V_{MP}^{∞} is the partial molar volume of a monomer at infinit dilution, N is the number of monomers per polymer (i.e. degree of polymerization) and v is the universal scaling exponent. This model was tested for water activity of PEG1000 + Na_2SO_4 + H_2O and PEG8000 + Na_2SO_4 + H_2O systems. These data were obtained by isopiestic method[3]. The agreement between the predicted and the experimental data is good.

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Characterisation of the structural and dynamical behaviour of curved interfaces of simple fluids in free-film, slit-like and cylindrical pore systems by Molecular Simulation.

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It is well known, that a gas when confined to a pore space of several molecular diameters may undergo a phase transition resulting inhomogeneous layered fluid-surface films and a highly curved, meniscus-like fluid-gas interface. How closely the structure and dynamical properties of the confined interfaces relate to those of the free liquid-gas interface is much less well known. In this paper we report a systematic study of the properties of the free-film and confined fluid interfaces. In particular we compare the surface tension and surface diffusion of the free-film and the confined liquid-gas interfaces.

The comparison of molecular dynamics simulations with the picture of hydration of non-electrolytes obtained from IR and NMR measurements.

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In aqueous mixtures of dimethyl sulfoxide(DMSO), acetone and 1,4-dioxane, we studied so far the concentration and temperature dependences of ^{1}H and ^{13}C chemical shifts in NMR and of the frequency for the C-H stretching vibration bands in IR spectra[1,2]. We measured NMR chemical shifts by the double reference method, by which we can measure chemical shifts, even at different concentrations or temperatures, with respect to the signal of a reference substance at a fixed reference state. In other words, since the chemical shifts are measured on a unified scale even under different measuring conditions, we can compare them strictly with each other.

From the results obtained we proposed a hydration mechanism for the alkyl moiety in the solutes, in which hydrogen-bonding basicity of the hydrophilic groups plays a decisive role to induce the polarization of the water molecules around solutes.

In this work, we carried out molecular dynamics simulations of the hydration of DMSO, acetone, and 1,4-dioxane using WinMASPHYC Pro. The results are discussed in terms of the effect of the basicity of the polar groups on hydration of the solutes, and are compared with the experimental results obtained from NMR and IR measurements.

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CONDUCTOMETRIC STUDY OF MAGNESIUM SULPHATE IN WATER FROM INFINITE DILUTION TO SATURATION

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Electric conductivities of magnesium sulphate at concentration from 10^{-4} to 2.5 mol dm^{-3} in water were measured from 5 to 35° C. The measurements on solution conductivity and density were carried out on highly pure products and in an inert atmosphere with an equipment yield precise data.

The Fuoss-Justice equation for associated electrolytes based on the Chemical Model of electrolyte solutions is applied to yield association constants and limiting conductivities. The limiting ionic conductivities λ_0^+ and λ_0^- are used by data analysis with the help of the MSA equation [1-3]. Data analysis is executed with two parameters which are fitted by least square fits on the measured data. Comparison to the lcCM (low concentration chemical model) is made.

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Cluster Analysis of HF / KF Mixtures

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Solutions of KF in liquid HF present remarkable features, since they are an example of ionic liquid whose properties are intermediate between solutions and molten salts. Moreover this system is the basic medium for the electrochemical production of fluorine. Since the experiments are difficult in such an aggressive medium, computer simulations are required to correlate, intrapolate and extrapolate available data.

In this work a classical statistical mechanical model is presented which allows for the evaluation of transport coefficients and can be understood in terms of (HFn)(n-1) clusters.

The results are in agreement with available experimental data and ab initio MD simulations.

Volumic properties of lithium perchlorate and *tetra*-ethylammonium bromide solutions in organic approtic solvents.

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Abstract

Lithium perchlorate has been used to prepare electrolytic solutions which have shown very good electrochemical qualities to prepare high energy batteries, specially where organic solvents of high permitivities and low melting points are demanded [1- 3].

This paper is concerned with apparent and partial molar volumes which have been calculated from density measurements of lithium perchlorate and *tetra*-ethylammonium bromide solutions in different approtic solvents. The experiments were performed at 25°C ± 0.01°C within the concentration range 1×10^{-2} to 3×10^{-2} mol dm^{-3}.

The variation of apparent molar volumes with molar concentrations obey to the Masson's equation [4, 5].

A thermodynamic analysis of the results was developed and, as a result, a discussion based on ion-ion, ion-solvent and ion-ion-solvent interactions is presented.

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Structural Effects on the Partial Molar Volume of Phosphonium and Ammonium Salts in Organic Solvents

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This work is concerned with the determination of apparent molar volumes for dilute solutions of tetraethylammonium and tetraethylphosphonium iodides in a variety of polar solvents, both protic and aprotic, at 25 °C.

Pitzer equation (1) as well as the Redlich-Rosenfeld-Meyer equation (RRM) (2) were tested to decribing apparent molar volume as a function of molal concentration. As both salts have a common anion the partial molar differences essentially reflect cationic differences which show interesting solvent-solute dependences. Such phenomena were interpreted in terms of structural cation adjustement in relation to the shape of solvating molecules.

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Complexes of Vanadium in Oxidation States from II to V formed in Molten Chlorides: An Electronic Absorption Spectroscopy Study

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Molten salts have a wide range of often unique properties which determine their potential use in various fields of modern technology. The rational use of molten salt-based systems requires a deep knowledge of their properties, including speciation of dissolved transition metal complexes.

In the present work we have investigated complex ions of vanadium, containing the metal in different oxidation states (II, III, IV and V), formed in alkali metal chloride-based melts under a variety of conditions. Studies were performed using electronic absorption spectroscopy, with some of the measurements being carried out by a reflection-absorption technique. The melts employed were NaCl-CsCl eutectic (at 550 - 700 °C) and NaCl-KCl equimolar mixture (at 680 - 980 °C), with the spectra recorded between 4,000 to 33,000 cm^{-1}. Samples for the spectroscopy measurements were prepared by dissolving "pre-prepared" concentrated samples in the solvent melt; by anodic dissolution of vanadium metal; and by reacting vanadium metal and oxides with chlorine or hydrogen chloride in the spectroscopy cell. The recorded spectra were (where necessary) resolved into individual component bands and analysed according to crystal field theory. The final products of the reactions were characterised by chemical analysis (including oxidimetric determination of the "mean" oxidation state of vanadium), and quenched melts were also analysed by X-ray powder diffraction.

Anodic dissolution of vanadium has been studied in NaCl-KCl melts at various anodic current densities. Vanadium dissolves, forming V(II) ions, at current densities of 100-150 mA cm^{-2}; increasing the current density above *ca.* 340 mA cm^{-2} leads to the formation of predominantly V(III) species.

Reactions of vanadium metal and vanadium oxides (V_2O_3 and V_2O_4) with hydrogen chloride or chlorine were followed by *in situ* spectroscopy measurements. Depending on the experimental conditions a range of vanadium chloro- and oxychloro-complexes is formed. Reaction of the V(III) chloro-complex with oxygen leads to the formation of VO(II) complex ions. Preliminary results indicate that the vanadium(IV) chloro-complex, VCl_6^{2-}, can be formed by oxidising VCl_6^{3-} with chlorine. Vanadium(V) oxide reacts with hydrogen chloride in NaCl-KCl melts, forming an oxygen-containing complex of vanadium(III); upon increasing the temperature from 680 to 980 °C the maximum in the spectrum is shifted from 14,300 to 15,600 cm^{-1}. Direct dissolution of V_2O_5 in NaCl-KCl melts results in the formation of sodium polyvanadate, NaV_6O_{15}.

HYDRATION OF *N*-OCTANOYL-*N*-METHYLGLUCAMINE MICELLES BY LIGHT SCATTERING, SMALL-ANGLE X-RAY SCATTERING, AND MOLECULAR DYNAMICS SIMULATION

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Dynamic light scattering (DLS) measurements have been made at 7 different temperatures (25 – 55 ℃) on aqueous solutions of *N*-octanoyl-*N*-methyglucamine (MEGA-8), which is a non-ionic surfactant with 5 hydroxyl groups and thus the critical micelle concentration as high as 69 mmol/kg, at various MEGA-8 concentrations (0.1 – 0.5 mol/kg). Small-angle X-ray scattering (SAXS) using synchrotron radiation has also been measured at an ambient temperature on aqueous MEGA-8 solutions of concentrations of 0.1 to 2.0 mol/kg. Based on the DLS and SAXS data, molecular dynamic (MD) simulation has been performed on a system of 49 MEGA-8 molecules and 5400 water molecules. Characteristic features of the MEGA-8 micelles in aqueous solutions will be discussed on concentration- and temperature-dependent structure (shape, size, aggregation) in terms of the hydrodynamic radius and the radius of gyration based on the LDS and SAXS data, the microscopic structure of hydration of the micelles and the dynamic properties of water molecules hydrated the micelles from the MD data.

A Raman Study of Aqueous Inorganic Salt Solutions in Liquid and Glassy States

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To get information about the strength of hydrogen bonds in aqueous electrolyte solutions, we have measured Raman OD (OH) stretching spectra of various aqueous electrolyte solutions as a function of salt concentration.

All aqueous salt solutions were prepared by dissolving an inorganic salt in a mixture of D_2O and H_2O. The final solution composition was set to be $M \cdot R(0.05D_2O \cdot 0.95H_2O)$ where M represents an inorganic salt and R is the molar ratio of water to salt.
Raman spectra were obtained with a JASCO NR1800 Raman spectrometer equipped with a microscope and a CCD detector, using ~100mW of 514.5 nm line of a Lexcel argon ion laser as an exciting source.

Uncoupled OD Raman stretching spectrum was decomposed into two Gaussian components using a least-squares curve fitting method. The frequency change of the lower frequency component with R is shown in Fig. 1. It is found that aqueous solutions are classified into two groups according to the frequency changes with R. The results indicate that the frequency of the uncoupled OD stretching Raman band is greatly dependent on the properties of both cation and anion.

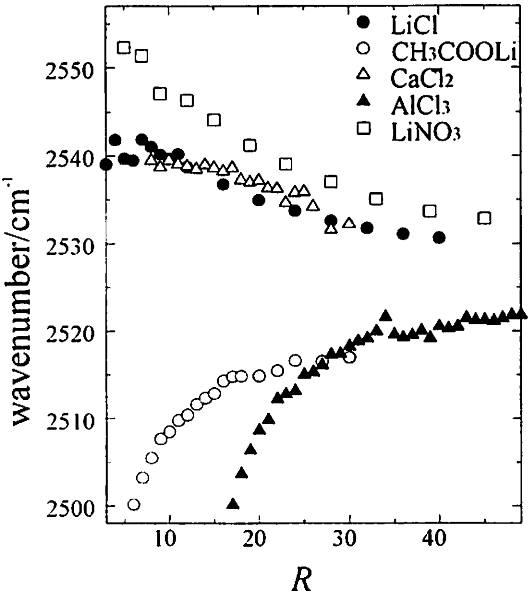

Fig. 1 The frequency change of the lower frequency component with R

MICROSCOPIC STRUCTURE OF CLUSTERS FORMED IN HEXAFLUOROISOPROPANOL-WATER MIXTURES

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Alcohol-water binary solutions have recently been revisited in biophysics and biochemistry fields, such as alcohol-induced α-helix promotion of peptides and proteins. In particular, 1,1,1,3,3,3-hexafluoro -2-propanol (HFIP) has been found to be most effective in stabilizing the α-helical structure among any alcohol available.[1] We have recently reported from a circular dichroism study that the microscopic structure of clusters in ethanol-water mixtures is closely related to denaturation of chymotrypsin inhibitor 2.[2] It is thus anticipated that the microscopic structure of clusters formed in HFIP-water binary solutions is responsible for their strong α-helix stabilization of peptides and proteins.

In the present study, the structure and dynamic properties of aqueous mixtures of HFIP have been investigated at room temperature over a whole range of HFIP mole fraction by large-angle X-ray diffraction (LAXS), small-angle neutron scattering (SANS), mass spectrometry, ^{13}C-NMR chemical shift, and ^{17}O-NMR relaxation. The LAXS data have shown that the hydrogen-bonded network of water persists at low HFIP concentrations ($x_{\mathrm{HFIP}} \leq \sim 0.1$) and that the structure of neat HFIP gradually predominates with increasing HFIP concentration at $x_{\mathrm{HFIP}} \geq \sim 0.15$. The Ornstein-Zernike plots of the SANS data have revealed that concentration fluctuation becomes largest at $x_{\mathrm{HFIP}} \sim 0.1$ with a correlation length ~9 Å. The mass spectra of cluster fragments generated in vacuum from HFIP-water mixtures showed that at $x_{\mathrm{HFIP}} = 0.09$ and 0.20 predominant clusters are A_1W_n ($n < 12$), where A and W represent HFIP and water molecules, respectively, as well as water clusters W_n ($n = 5\sim8$) and that oligomers of HFIP are formed only at low x_{HFIP} 0.005~0.1. The ^{13}C chemical shifts of both CF_3 and CH groups of HFIP have an inflection point at $x_{\mathrm{HFIP}} \sim 0.1$ for the HFIP-water mixtures. The ^{17}O relaxation data showed that the orientational motion of water molecules is rapidly retarded with increasing x_{HFIP} to ~ 0.1 and becomes constant at $x_{\mathrm{HFIP}} > \sim 0.3$. From all information obtained in the present study, the most likely models are proposed for aggregation of HFIP and water molecules in the HFIP-water mixtures.

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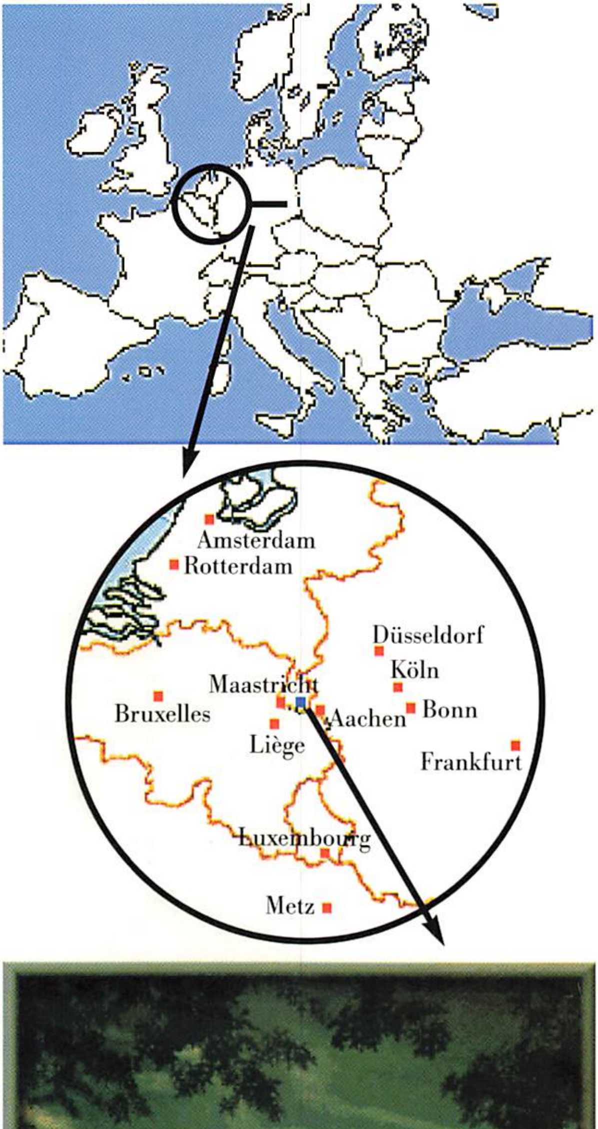
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