TOSHIO YAMAGUCHI

IUPAC / International Year of Chemistry 2011
32nd International Conference on **Solution Chemistry**
La Grande Motte, France, Aug. 28th – Sep. 2nd 2011

IUPAC
International Union of Pure and Applied Chemistry

International Year of CHEMISTRY 2011

MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE

cea

um2

32nd International Conference on Solution Chemistry

Book of abstracts

ICSC2011
La Grande Motte, France
August 28th – September 2nd 2011

ICSC

IUPAC / International Year of Chemistry 2011

32nd International Conference on **Solution Chemistry**

La Grande Motte, France, Aug. 28th – Sep. 2nd 2011

IUPAC
International Union of Pure and Applied Chemistry

International Year of CHEMISTRY 2011

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE
MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE

cea

um2
UNIVERSITÉ MONTPELLIER 2

PÔLE Chimie Balard

32nd International Conference on Solution Chemistry

Book of abstracts

ICSC2011
La Grande Motte, France
August 28th – September 2nd 2011

Table of contents

Welcome at the 32nd International Conference on Solution Chemistry

Forewords

On behalf of the organizing committee, we wish to welcome you to the 32nd International Conference on Solution Chemistry (ICSC), to be held in La Grande Motte, France, from the 28th of August to the 2nd of September 2011. We are happy to be receiving over 170 participants, from all continents (expect Antartica!), to help celebrate the International Year of Chemistry (IYC2011) on the Mediterranean Coast, at the border of the beautiful Camargue, which is one of the last remaining natural sites in France.

The conference will cover all aspects of current solution chemistry: theoretical, experimental, simulations, and practical applications. This research is more necessary than ever, as it holds the keys to solving some of the most pressing economic, energetic, and environmental challenges we face today (even though funding seems to be increasingly difficult to obtain). In particular, in the field of solutions, the dramatic rise in the water needed for human and agricultural use, along with the ever-growing list of pollutants contributing to its contamination, has made the treatment and storage of wastes a fundamental issue in any industrial process. To meet these global challenges, we require a better understanding of the physicochemical behavior of solutions, as evidenced by the recent advances in "green" chemistry.

We are eager to welcome all participants in La Grande Motte and hope you will enjoy both a great conference and a pleasant area.

Professor Pierre Turq
Chairman of the Organizing Committee

Program

Keynote presentations last 30 mn and oral presentations last 20 mn, including questions.
The page number (column 2) is the one of the corresponding abstract in this book of abstracts.

Sunday 28th

From 12:00 Registration and dinner

21:00 Opening Session in Room A

chair: J.-F. Dufrêche

Starts at	page	
21:00		**Welcome at La Grande Motte for the 32nd ICSC** *TURQ, Pierre*
21:15	20	**Most food are... aqueous solutions** **(International Year of Chemistry conference)** *THIS, Hervé*

Monday 29th

8:40 Plenary Lecture in Room A

chair: T. Yamaguchi

8:40	22	**Ultrafast UV and X-ray studies of chemical and biological systems** *CHERGUI Majed*

9:30 Coffee Break

10:00 Parallel Sessions

Room A

chair: V. Vlachy

10:00	121	**Influence of solution composition on ion binding with heparin and dextran sulphate** *BARTCZAK, Martyna*
10:20	50	**Interaction between charged surfaces mediated by molecules with spatially distributed charges** *BOHINC, Klemen*
10:50	88	**Aqueous solutions of hydrophilic and hydrophobic amino acids**

		TEIXEIRA, José
11:20	94	**Exploring Life Phenomena with a Statistical Mechanics of Molecular Solution** *HIRATA, Fumio*
11:50	96	**Cationic liposomes as gene delivery vehicles: the structure and binding capacity** *UHRIKOVA, Daniela*

Room B

chair: M. Jardat

10:00	54	**A new insight into structures of concentrated associated salt aqueous solutions: combination of thin-film Ultra-violet spectroscopy and TD-DFT calculation** *ZENG, Dewen*
10:20	57	**A Computational Approach to Solvent Properties; Measures of Lewis acidity and Basicity** *WAGHORNE Earle*
10:40	63	**Reaction Thermodynamics for Ionization of Acetic Acid in Protic Ionic Liquid, Ethylammonium Nitrate** *KANZAKI, Ryo*
11:00	73	**Acid solubilisation into hydrophobic ionic liquids: role of TBP co-solvent investigated by experiments and simulation** *GAILLARD, Clotilde*
11:20	86	**Friedman's Excess Free Energy and the McMillan-Mayer Theory of Solutions** *GóMEZ-ESTéVEZ, Juan Luis*
11:50	91	**Adsorption and Dynamics of Water and Ions in Nanopores** *COASNE, Benoit*

14:00 Parallel Sessions

Room A

chair: P. Madden

14:00	79	**Lewis basicity scales in liquids from first-principles** *SALANNE, Mathieu*
14:30	36	**Multiscale modeling of solvation in chemical and biological nanosystems and nanoporous materials** *KOVALENKO, Andriy*
15:00	55	**Molecular models of natural organic matter and its colloidal aggregation in aqueous solutions: Challenges and opportunities for computer simulations** *KALINICHEV, Andrey*
15:30	75	**Diffusion and partitioning of some organic molecules and ions in aqueous micellar solutions** *TOMINAGA, Toshihiro*

Room B

chair: M.-C. Charbonnel

14:00	53	**The role of water in conformational transitions of peptides**

		NERUKH, Dmitry
14:20	61	**Insights into the interaction of some antibiotic drugs with serum albumin: Biophysical aspects** *CHOUDHARY, Sinjan*
14:40	62	**Quantitative and qualitative characterization of the partially folded states of proteins: Calorimetric and spectroscopic investigation** *SHARMA, Nand Kishore*
15:00	78	**Effect of glucose on the volumetric behavior of some amino acids in aqueous media at different temperatures** *JAMAL, Muhammad Asghar*
15:20	30	**Kinetics and Thermodynamics of Cd(II) Ions Sorption on Mixed Sorbents Prepared from Olive Stone and Date Pit from Aqueous Solution** *LOUHAB, Krim*
15:40	48	**Physico-Chemical and Structural Characterization of the Binary System Phosphoric Acid – N,N-dimethylformamide** *FADEEVA, Yuliya*

16:00 Coffee Break

16:30 Parallel Sessions

Room A

chair : B. Coasne

16:30	87	**Fluids in porous media :Theory and computer simulations.** *HOLOVKO, Myroslav*
17:00	101	**Zeta potential, surface properties and flocculation behaviour of colloidal clay** *CHASSAGNE, Claire*
17:30	72	**Use of microcalorimetry to determine the enthalpies of solid-solution exchanges** *MOREL-DESROSIERS, Nicole*

Room B

chair: A. Kalinichev

16:30	91	**Speciation of uranyl nitrate in organic phases containing monoamide extractant** *FERRU, Geoffroy*
16:50	74	**Behavior of hydrophobic ions in aqueous medium** *BHOWMIK, Debsindhu*
17:10	65	**Electrophoretic NMR - methodology and some applications** *STILBS, Peter*

18:00 International Year of Chemistry Session in Room A

chair: N. Morel-Desrosiers

18:00	21	**The Chemistry of Water-logged Archaeological Wood (International Year of Chemistry conference)** *PERSSON, Ingmar*

Tuesday 30th

8:30 Plenary Lecture in Room A

chair: Y. Marcus

8:30	23	**From Specific Ion Effects to New Ionic Liquids** *KUNZ, Werner*

9:20 Coffee Break

Parallel Sessions

Room A

chair: M. Holovko

9:50	29	**Water structure enhancement in water-rich mixtures with organic solvents** *MARCUS, Yizhak*
10:20	58	**The Use of Models to Understand the Chemistry of Actinoids** *VITORGE, Pierre*
10:50	45	**Generalized excluded volume: its origin and effects** *NEZBEDA, Ivo*
11:20	85	**Thermochemistry related to the liquid-liquid extraction of cations** *CHARBONNEL, Marie-christine*
11:50	71	**Stucture and dynamicsof a lihium ion in ionic liquids: towards high safety batteries** *UMEBAYASHI, Yasuhiro*

Room B

chair: D. Borgis

9:50	66	**Accurate force fields from ab-initio simulations : The case of aqueous ions** *ROTENBERG, Benjamin*
10:20	101	**Solvation of silver in saline hydrothermal fluids from first-principle molecular dynamics** *VUILLEUMIER, Rodolphe*
10:50	64	**Excess Electrons in Water: What Can We Learn from Molecular Dynamics Simulations?** *TURI, László*
11:20	99	**A new model for the stability and mobility of finite colloidal concentration** *LOZADA-CASSOU, Marcelo*
11:50	97	**Cellular Automata Approach to Corrosion and Passivation Phenomena** *STAFIEJ, Janusz*

14:00 Parallel Sessions

Room A

chair: I. Nezbeda

14:00	84	**Dynamic properties of charged nanoparticles in solution from coarse-grained simulations** *JARDAT, Marie*
14:30	82	**Thermodynamics of aqueous solutions of aliphatic ionenes with halide**

		counterions *VLACHY, Vojko*
15:00	34	**Time-Resolved Translational Diffusion Reveals Kinetics of Reaction Intermediates of Biological Proteins** *TERAZIMA, Masahide*
15:30	100	**Role of non-ideality for the ion transport in porous media: derivation of the macroscopic equations using upscaling** *MIKELIC, Andro*

Room B

chair: E. Dubois

14:00	61	**Properties of Hydrated Alkali Metal Ions in Aqueous Solution** *MäHLER, Johan*
14:20	65	**A Study of Allowed Electronic Transition of Organic liquid by using Attenuated Total Reflection in Far-Ultraviolet region: ~structure of liquid and electronic transition~** *MORISAWA, Yusuke*
14:40	68	**Structural heterogeneity and anomalous hydrogen bonding in a series of primary alkylammonium nitrate ionic liquids revealed by High-energy X-ray diffraction experiments and MD simulations** *SONG, Xuedan*
15:00	68	**Efficient gold extraction from water by use of ionic liquids** *VITE, Ghislain*
15:20	83	**The effect of solvent molecule and co-existing alkali cation on the luminescence of tris (oxalato) chromate(III) and tris(malonato)chromate(III) in the glassed mixed-solvent of water and ethanol at 77 K.** *OTSUKA, Takuhiro*
15:40	87	**Cryo-brines - a new field for solution chemistry?** *VOIGT, Wolfgang*

16:00 Coffee Break

16:30 Parallel Sessions

Room A

chair: M. Terazima

16:30	98	**Dynamics and reactivity in confined media : From micropores to macropores** *RENAULT, Jean Philippe*
17:00	103	**Oral de JFD/Thomas ZEMB** *ZEMB, Thomas*
17:30	90	**Ultrasoft primitive model of polyelectrolytes in solution** *COSLOVICH, Daniele*

Room B

chair: R. Vuilleumier

16:30	31	**Possibilities of differential scanning calorimetry method to identify carbon nanomaterials** *AVRAMENKO, Natalia*

16:50	63	**Nitrate Coordination with Eu3+: influence of the solvent on the nature of the ion pair** *GUILBAUD, Philippe*
17:20	45	**Formation and testing of honge oil as a biodiesel** *PARASHAR, Amit*
17:40	105	**A novel concept for augmented van der Waals equation of state** *TROKHYMCHUK, Andrij*

18:00 - 19:30 Poster Session

Wednesday 31th

8:40 Plenary Lecture in Room A

chair: M. Klein

8:40	24	**Modeling Ionic Liquids** *MADDEN,Paul*

9:30 Coffee Break

10:00 Parallel Sessions

Room A

chair: C. Chassagne

10:00	41	**From Molten Salt to Electrolyte Solution: Dynamics of Ionic Liquids and their Mixtures** *BUCHNER, Richard*
10:30	85	**Vibrational spectral diffusion and molecular motion in supercritical water and aqueous solutions** *CHANDRA, Amalendu*
11:00	94	**How well-behaved are electrolyte mixtures at high temperatures ?** *HEFTER, Glenn*
11:30	102	**Molecular Density Functional Theory of Solvation: From polar solvents to water** *BORGIS, Daniel*
12:00	103	**High temperature solubility of lanthanide halides in alkali metal halide melts.** *GAUNE-ESCARD, Marcelle*

Room B

chair: J. Aupiais

10:00	103	**Towards a simple theory of the viscosity of electrolyte solutions: a mode-coupling approach** *MOLINA, John*

10:20	56	**On the use of high precision conductimetry of ionic mixtures to determine the effective charge and size of nanocolloids: Application to the complexation by humic substances of small cations.** *MéRIGUET, Guillaume (UPMC)*
10:40	60	**Apparent Molal Volumes of 1,3,5,7-Tetraazatricyclo[3.3.1.1(3,7)]decane and 1,4,6,9-Tetrazatricyclo(4.4.1.1.4,9)dodecane in Aqueous Solution as a Function of Temperature** *VARGAS, Edgar*
11:00	60	**Enthalpies of solution of Calix[4]resorcinarene in non-aqueous solvents as a function of concentration and temperature** *RIVEROS SANTOYA, Diana Carolina*
11:20	70	**Thermodynamic peculiarities and phase diagrams of quaternary solutions with chemical reactions and miscibility gap: critical states, phase and chemical equilibria** *TOIKKA, Maria*
11:40	89	**Standard State Thermodynamic Properties for Ionization of Water up to 5715 K** *DJAMALI, Essmaiil*
12:00	51	**Unravelling hydration properties of lanthanoids and actinoids cations in water: an interplay between experiments and theory** *SPEZIA, Riccardo*

14:00 Parallel Sessions

Room A

chair: I. Billard

14:00	111	**Experimental study of regularires in the rare earths hydrolytic behaviour** *STEPANCHIKOVA, Sophia*
14:30	42	**Mobility of water molecules in ion hydration shells and dielectric spectroscopy data in whole orientation frequency range** *LYASHCHENKO, Andrey*
15:00	93	**Mobility of charged colloids by electroacoustics** *DUBOIS, Emmanuelle*
15:30	77	**Possible routes for pyrochemical separation** *DELPECH, Sylvie*

Room B

chair: G. Hefter

14:00	105	**Understanding radionuclide chemistry and transport in clay-rich materials - a key element for demonstrating the safety of underground disposal facilities in clay-rock formations** *ALTMANN, Scott*
14:20	72	**Sharp decrease of the dielectric friction on polyions during conformation transition from pearl-chain to coiled shapes** *MHALLA, Jalel*
14:40	59	**An Experimental Atomistic Study of the Cryoprotectant Glycerol in Aqueous Solutions**

		TOWEY, James
15:00	32	**The formation of supramolecular structures in organic solvents** *GREENWALD, Iosif*
15:20	53	**Sorption of gold(III) on mercapto modified rice hull ash silica** *NURYONO, Nuryono*
15:40	55	**Effect of CaCl2 on the Self Aggregation of Serotonin Norepinephrine Reuptake Inhibitor drug Venlafaxine HCl over Temperature Range 298.15-313.15 K** *JAMAL, Muhammad Asghar*

16:00 Coffee Break

16:30 Parallel Session

Room A

chair: R. Buchner

16:30	92	**Transport and thermodynamic properties of complex mixed electrolytes : Modeling within the Mean Spherical Approximation** *BERNARD, Olivier*
17:00	96	**Some apsects of organic Chemistry in super heated water** *GOETTMANN, Frédéric*
17:30	46	**Calorimetric determination of enthalpy changes for the proton ionization of 3-[N-morpholino]propanesulfonic acid (MOPS), 4-[N-morpholino] butanesulfonic acid (MOBS) and 3-[N-morpholino]-2-hydroxypropanesulfonic acid (MOPSO) in water-methanol mixtures** **JUMEAN, Fawwaz**

Room B

chair: J. Mhalla

16:30	60	**Extraction and quantification of organic phosphorus in compost, soil and sediment** *PARASKOVA, Julia*
16:50	67	**Multiscale modeling of ionic transport in charged clays** *DUVAIL, Magali*
17:10	76	**Mesoscopic structures induced by the solvation effect of antagonistic salts in the mixture of water / organic solvent** *SADAKANE, Koichiro*
17:30	36	**Measurement of the pure dissolution rate constant of a soft mineral in water** *COLOMBANI, Jean*

18:00 - 20:00 "Poyster" Session

Thursday 1st

8:30 Plenary Lecture in Room A

chair: F. Hirata

8:30	26	**Diffusion-reaction in micro- and nano-confined spaces** *AMATORE, Christian*

9:20 Coffee Break

9:50 Parallel Sessions

Room A

chair: M. Bester Rogac

9:50	57	**Leaching of sulfide ores with solutions containing natural organic acids** *NOVIKOVA, Svetlana*
10:10	74	**Structure, properties of water and new approaches to assessment of drinking water quality** *GONCHARUK, Vladyslav*
10:30	79	**Time evaluation of aqueous leachates composition from pyrite and gossan wastes amended with organic and inorganic materials. Pot experiments** *ABREU, Maria Manuela*
10:50	46	**Electrophoretic mobility and speciation: experiments, interpretation and problems** *AUPIAIS, Jean*
11:20	81	**Arsenic in natural aqueous systems. What a challenge!** *MAGALHãES, Maria Clara*

Room B

chair: A. Chandra

9:50	84	**Computational Studies of Self-Assembly: From Surfactants and Janus Dendrimers to Ionic Liquids and More** *KLEIN, Michael*
10:20	29	**Spatial decomposition analysis of protein thermodynamics based on the 3D-RISM theory** *YAMAZAKI, Takeshi*
10:50	35	**A transferable model of water** *BARANYAI, András*
11:20	77	**Conductivity of electrolyte solutions-an outdated story ?** *BESTER ROGAC, Marija*

13:00 Departure for Conference Excursion

13:00-23:00 Conference Excursion & Conference Dinner

Pont du Gard – Avignon – Palais des Papes

Friday 2nd

8:30 Plenary Lecture in Room A

chair: M. Lozada-Cassou

8:30	27	**Structure and Dynamics of Liquids and Solutions in Confinement** *YAMAGUCHI, Toshio*

9:20 Coffee Break

9:50 Parallel Sessions

Room A

chair: J. Teixera

9:50	95	**Phase equilibria of binary and ternary systems containing ILs** *ROONEY, David*
10:20	43	**Thermodynamic and structural investigation of the trivalent actinides complexation with DTPA** *LEGUAY, Sébastien*
10:40	44	**Towards a more comprehensive modelling capability for aqueous solution thermodynamics** *ROWLAND, Darren*
11:00	47	**Enthalpies of Solution of 1,3,6,8-Tetrazatricyclo [4.4.1.13,8]dodecane as function of concentration and temperature** *SALAMANCA BLANCO, Yina Patricia*
11:20	120	**Heats of Mixing in Binary Liquid Alloys of Transition Metals** *DUBININ, Nikolay*
11:40	52	**Study of the EDTA speciation for its quantification in radioactive wastes containing heavy metals** *RENAUDIN, Laëtitia*

Room B

chair: K. Bohinc

9:50	33	**Synthesis and Characterization of Three Novel Resins** *FALLAHI, Afsoon*
10:10	34	**Study of Chain Length Effect on Dielectric Relaxation and Thermodynamic Properties of Polymers Using TDR Method** *SARODE, Arvind*
10:30	47	**Synthesis and Preparation of Diethanolamine Functionalized Monodisperse Nanoporous Poly(HPMACl- EDMA) for Hydrophilic Interaction Chromatography** *DİNÇ, Salİha*
10:50	51	**X-ray and neutron scattering study of aqueous solutions of polyhydroxycompounds** *SHALAEV, Evgenyi*
11:10	89	**Chemical template synthesis of polypyrrole nanowire arrays and their hydrogen gas sensing properties** *OMIDVAR, Hamid*

11:30	99	**Study of random amphiphilic polyanions for molecular encapsulation of water-insoluble compounds** *SCHOTT, Marc-alexandre*

Poster Sessions

Poster session 1

Tuesday 30th, 18:00-19:30

p.	
107	**The influence of ionic strength on the equilibrium constant of vanadyl(IV), O-S anionic ligand of D-penicillamine** *HAKIMELAHI, Rakhshan*
108	**Toward fragment-based drug design using a new ligand-mapping method based on molecular liquid theory** *IMAI, Takashi*
109	**The influence of anthropogenic drainage waters on adjacent area soil composition** *NOVIKOVA, Svetlana*
109	**Hydrophobic effect on the conformational equilibria of diethyl ether and ethyl isopropyl ether using Raman spectroscopy and molecular dynamic simulation** *WADA, Ryoichi*
110	**Transference Number and Conductance Studies of Sodium Chloride in 20 Mass per cent Ethanol + Water, and 20 Mass per cent Formamide + Water Mixture at 298.15 K** *TOMAš, Renato*
111	**Stepwise formation of the molecular complexes of 3-nitrofluoranthene with toluene in cyclohexane** *KOBAYASHI, Michio*
112	**Photo-induced Electron Transfer Reaction between Aromatic Compounds in Ethylene Glycol** *INADA, Taeko*
113	**Shape changes in polysorbate 20 micelles of nanoscale self-assembly in aqueous solutions of each of three polar solvents (1,4-dioxane, dimethyl sulfoxide, N,N-dimethylformamide).** *AIZAWA, Hideki*
113	**The anion influence on hydrophobic hydration of tetraalkylammonium hydroxides and salts** *LYASHCHENKO, Andrey*
114	**Complexation of protactinium(V) with citric and nitrilotriacetic acids** *LEGUAY, Sébastien*
115	**Interparticle Interactions from Activity of Water of Ternary Amino Acid-Electrolyte Solutions** *TSURKO, Elena Nikolayevna*
116	**Hydration and microwave dielectric properties of alkali metals and ammonium fluorides** *LILEEV, Alexander*
117	**Sensitive separation and characterization of plants extracts for discovery of new anticancer leaders** *IONKOVA, Iliana*
117	**Electrophoretic mobility of some isotopes in aqueous solution at 25 °C and infinite**

	dilution from conductivity data and/or capillary electrophoresis *AUPIAIS, Jean*
118	**Critical and limiting fluxes in ultrafiltration using a porous polymeric tubular membrane** *BEICHA, Abdellah*
118	**Hard convex body fluids confined in random porous media: scaled particle theory** *HOLOVKO, Myroslav*
119	**Ionic Association and Solvation of the Ionic Liquid 1-Hexyl-3-Methylimidazolium Chloride in Molecular Solvents Revealed by Vapor Pressure Osmometry, Conductometry, Volumerty and Acoustic Measurements** *SADEGHI, Rahmat*
120	**Conductance of potassium chloride in methanol at high temperatures and pressures up to 473 K and 100 MPa** *HOSHINA, Taka-aki*
48	**ATR-IR study on the concentration dependence of hydration number of alkali metal ions** *KAMEDA, Yasuo*
49	**Terahertz spectroscopy study of concentrated sorbitol solutions and glasses** *SIBIK, Juraj*
121	**The Structure in Water-Alcohol Mixtures by Monte Carlo Method** *ATAMAS, Nataliya*
122	**Temperature effects on reorientational correlation time of water in formamide and N,N-dimethylformamide - water mixtures** *OKADA, Masaki*
123	**An Infrared and Computational Study of Hydrogen Bonding to Uracil Maryam Hajimohammadpour and Earle Waghorne** *HAJIMOHAMMADPOUR, Maryam*
123	**Hydrolysis Aqueous Sulfu and at Moderately pH ric Acid of Poly(e-caprolactam) at High pH** *MANTECA-DIEGO, Consolacion*
124	**Estimation of the "hydrophobic reactivity" of SDS by the use of BPh4- anions** *BOUGHAMMOURA, Sondès*
125	**An Infrared and Computational Study of Hydrogen Bonding to Uracil** *HAJIMOHAMMADPOOR, Maryam*
126	**Structure and dynamics of CO2, H2CO3, HCO3-, CO3(2-) in aqueous solutions: Ab initio molecular dynamics simulations** *KALINICHEV, Andrey*
126	**The structure of electrolyte solutions and dynamics of ions near single wall carbon nanotubes** *KOLKER, Arkady*
127	**Complexes of sulfuric acid with N,N-dimethylformamide: an ab initio investigation** *SAFONOVA, Liubov*

Poster session 2
Wednesday 31st, 18:00-20:00

p.	
128	**Physico-chemical properties of proton conducting electrolytes at confined geometry of polymeric gel** *SHMUKLER, Liudmila*
129	**Description of aqueous solutions of ammonium and bulky anions within the BiMSA model: Towards the description of ionic liquids in water** *PAPAICONOMOU, Nicolas*
129	**Comparative studies of hydration of some oxoanions** *EKLUND, Lars*
130	**The interaction of iron and oxygen on oak wood – determination of degree of deterioration of iron impregnated fresh oak wood by tensile strength and chemical analyses and comparison with Vasa wood** *JOHANSSON, Charles*
131	**Solution Properties and Cross-linking Reaction of Syndiotactic-like PVA Solution** *OH, Tae Hwan*
131	**NMR Relaxation Studies on 1-Alkyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)amide** *KANAKUBO, Mitsuhiro*
132	**Physicochemical Properties of Diglyme-Lithium Bis(trifluoromethanesulfonyl)amide Solutions** *KANAKUBO, Mitsuhiro*
132	**Absorption and Desorption Properties of CO2 in DBU-Alcohol Systems** *KANAKUBO, Mitsuhiro*
133	**Raman spectroscopic study on N-methylimidazolium based Protic Ionic Liquids** *UMEBAYASHI, Yasuhiro*
134	**Determination of Distance-dependent Viscosity of Mixtures in Parallel Slabs using Non-equilibrium Molecular Dynamics** *PAřEZ, Stanislav*
134	**Molecular simulations of electrokinetic phenomena at the solid-liquid interface** *PAřEZ, Stanislav*
135	**Experimental study and thermodynamic analysis of quaternary reacting systems with ester synthesis reaction in solution** *TOIKKA, Maria*
136	**Study of destruction of water structure in the binary mixtures N,N-dimethylformamid-water and tetrahydrofuran-water** *MIRZAEV, S.z.*
137	**Study of density and adiabatic compressibility fullurene (C60) solutions** *MIRZAEV, S.z.*
138	**Ion pairing of biologically important ions: A global model** *BONCINA, Matjaz*
138	**Effect of temperature on the sorption of Selenium on alumina and montmorillonite** *MOREL, Jean-pierre*
139	**Insights on capacitive and structural properties of [BMI][PF6] confined between**

	graphite electrodes from molecular dynamics *SALANNE, Mathieu*
140	**Acoustic, thermodynamic, and transport properties of aqueous solutions of sodium cyclamate at (298.15, 303.15, 308.15, and 313.15) K** *KHARAT, Sanjeevan*
140	**Predicting the Solubility of Alkali and Alkali Earth Halides by Artificial Neural Network** *TAURA, Toshiaki*
141	**Properties of Syndiotactic Poly(vinyl alcohol) Solution Containing Zirconium Oxide** *OH, Tae Hwan*
141	**Electrocatalytic oxidation of Acetaminophen on a Nanocamposit Ni- αAl2O3nickel modified Grafit electrode** *MIRZAPOURARMAKY, Abolfazl*
142	**Sorption of aluminium from drinking water by ion-exchangers of different chemical nature** *IAKYMOVA, Tetiana*
143	**The effect of anodizing parameters on morphology of TiO2 nanotube arrays** *OMIDVAR, Hamid*
143	**An analytical expression of the Ornstein-Zernike integral equation of hard-sphere liquid derived from the extended scaled particle theory** *IRISA, Masayuki*
144	**A comparison between the morphology of chemical and electrochemical template synthesized polypyrrole nanowires** *HASSANZADEH, Nafiseh*
144	**The effect of pressure on the trans-gauche equilibrium of n-butane in water: Relevance to pressure denaturation of proteins** *KATO, Minoru*
145	**Colloidal porous nanoparticles of vermiculite** *MIRZAEV, Sirojiddin*
145	**Scaled particle theory for one- and two- dimensional hard-core fluids in disordered porous matrices** *HOLOVKO, Myroslav*
146	**Molecular simulation of fluid-solid interface at nanoscale** *OULD-KADDOUR, Fouzia*
146	**Thermodynamic approach of actinides solvation and extractionby N,N-dialkylamide** *RODRIGUES, Florian*

ICSC 2011 La Grande Motte

Modeling complex biological systems: from solution chemistry to membranes

BAADEN, Marc (Laboratoire de Biochimie Théorique, CNRS, UPR9080, Univ Paris Diderot, Sorbonne Paris Cité), TEK, Alex (Laboratoire de Biochimie Théorique, CNRS, UPR9080, Univ Paris Diderot, Sorbonne Paris Cité) ; LAURENT, Benoist (Laboratoire de Biochimie Théorique, CNRS, UPR9080, Univ Paris Diderot, Sorbonne Paris Cité)

Some insights about modeling the solution chemistry of the GLIC ion channel and the membrane interactions of the SNARE complex involved in membrane fusion are presented.

Complex biological systems are intimately linked to their environment, a very crowded and equally complex solution compartmentalized by fluid membranes. Modeling such systems remains challenging and requires an accurate representation of these solutions and their interfaces. Here, we will focus on particle-based modeling either at an atomistic or a coarse grained level using molecular dynamics simulations. A first example illustrates the functional importance of solvation for an ion channel of the cys-loop receptor family, a major target of many drugs including anti-smoking compounds, muscle relaxants, potential Alzheimer disease treatments and anti-vomiting prescriptions used in chemotherapy. Next, biological membranes will be discussed, using the example of SNARE-mediated membrane fusion. SNAREs may induce and supporthigh tensions between adjacent membranes thereby modifying their interfaces. As an outlook, current challenges will be presented along with promising novel modeling approaches.

Coordination vs. molar volumes in amide solvated lanthanoid(III) ions

Daniel Lundberg,[a*] Anna Płaczek,[a] Dorota Warmińska,[b] and Ingmar Persson[a]

[a] *Dept. of Chemistry, Uppsala BioCenter, Swedish Univ. Agr. Sci.,*
P.O. Box 7015, SE-750 07 SWEDEN
[b] *Dept. of Phys. Chemistry, Chem. Fac., Gdańsk Univ. Technology,*
ul. Narutowicza 11/12, 80-233 Gdańsk, POLAND

Abstract: The strong suit for structural methods in solution are well-determined bond distances and coordination properties, while volumetric data can provide useful information on certain ion/solvent interactions; combined they should yield a more complete understanding of the studied systems. This coordination chemistry study combines results from X-ray absorption spectroscopy (XAS) and large angle X-ray scattering (LAXS) with those originating from partial standard molar volumes.

The investigation included three representative lanthanoid(III) ions and three structurally slightly different amides, allowing for a discussion on how steric hindering may affect coordination number. On the basis of a larger, previously performed study on all naturally occurring lanthanoid(III) ions,[1] it was shown that lanthanum(III), gadolinium(III), and lutetium(III) were solvated by a different number of solvent molecules depending on the ionic radius with additional differences due to the steric effects of the ligand.

The different solvation numbers revealed ought to be reflected in the values calculated for the molar volumes, where at least a qualitative analysis of ionic molar volumes should be possible.[2] Taking the different coordination numbers into account may help explain why the values of the molar volumes do not follow the expected pattern related to the decreasing ionic radius of the lanthanoid series.

1. D. Lundberg, I. Persson, L. Eriksson, P. D'Angelo, S. De Panfilis. *Inorg. Chem.* **49**, 4420-4432 (2010).
2. Y. Marcus. *J. Mol. Liq.* **118**, 3-8 (2005).

International Year of Chemistry (IYC) and Plenary Lectures Abstracts

Most food are... aqueous solutions
Recent results of Molecular Gastronomy.

THIS Hervé - IYC lecture

Most food are liquid... as most food are gels. Indeed human food today is primarily based on plant and animal tissues, i.e. systems made of cells, respectively plant cells or muscular fibers, dispersed in solids systems. The inside of cells is itself a gel, i.e. (according to IUPAC) a dispersion of a liquid in a solid, with at least the dimension of one kind of objects being of less than a micrometer. This is why our food can be studied using liquid frequency domain nuclear magnetic resonance spectroscopy. When vegetables, meat, fish, sauces, are put in a MNR tube and studied directly, with or without water suppression sequence, the « first order » composition of food can be studied, before or after thermal processing (« cooking »).
Using such tools, which kind of study can be done ? As the fielf of Molecular Gastronomy (the science which looks for the mechanisms of phenomena occurring during culinary transformations) is infinite, the French Group of Molecular Gastronomy worked focused on the study of processes of the kind M@E → M' @ E' (here M stands for the food matrix, E for its environment, and @ for inclusion, as recommanded by IUPAC. The interest of the new analytical method called *in situ* quantitative nuclear magnetic resonance spectroscopy (d q NMR), was investigated, and it was shown that this fast method was giving access to more saccharides than with conventional methods including extraction and quantitative determination of extract. Indeed this is not the sole advantage, as this method is much faster, and does not use any organic solvent.
In parallel, models were studied for various processes as classified using the complex disperse system/non periodical organisation of space formalism (« disperse systems formalism »).
Finally as an application of these studies, a new paradigm in cooking was promoted as "Note by Note Cuisine". This new developing trend asks many scientific, toxicologic, technical, technological, artistical and political questions.

The Chemistry of Water-logged Archaeological Wood

PERSSON, Ingmar (SLU) GUNNAR, Almkvist (SLU) - IYC lecture

The chemistry in the Swedish warship the Vasa, wrecked in 1628 and salvaged in 1961, has been studied in order to understand the weakening of its mechanical strength and the formation inorganic sulfate salts which started to precipitate on its surfaces in 2000. Iron compounds, present throughout the wood, seem to catalyze the decomposition of the conservation agent polyethylene glycol (PEG), and hemi-cellulose and cellulose into smaller molecular fragments in Fenton-like reactions. In the areas with high degree of decomposition relatively large amounts of formic, acetic, glycolic and oxalic acid have been detected. It is therefore important to reduce the iron content in the wood as much as possible. A method to extract the iron compounds from the wood using a strong complexing agent for iron compounds has been developed. Organic sulfur compounds seem to act as anti-oxidants preventing radicals to attack PEG and wood constituents as the decomposition is significantly lower in areas rich in reduced sulfur compounds. The chemical situation in the Vasa specifical¬ly, and for water- logged in general, and the chemical back-ground to the present situation will be presented as well as methods to improve the conservation of archaeological wooden artifacts.

Inter- and intramolecular dynamics in liquids: ultrafast optical and X-ray studies

CHERGUI, Majed
Lab. of Ultrafast Spectroscopy, Ecole Polytechnique Fédérale de Lausanne,
CH-1015 Lausanne, Switzerland

We will present recent ultrafast optical and X-ray absorption studies of the photoinduced structural dynamics as well as solvation dynamics in solutions. A combination of ultrafast fluorescence, transient absorption in the deep-UV and picosecond and femtosecond X-ray absorption spectroscopy[1] was used to study the ultrafast structure changes accompanying the intramolecular electron transfer in metal-based molecular complexes, emphasizing the role of the solvent in affecting these processes.[2,3,4] We will also present our recent results of the transition from hydrophilic to hydrophobic solvation upon electron abstraction from aqueous iodide.[5] The observations are supported by quantum-chemical calculations and by classical and quantum mechanical/Molecular mechanics (QM/MM) molecular dynamics simulations, which also show that hydrophobic solvation is determined by the time scale needed to form a network of hydrogen bonds in the solvation shell.

XFEL

X-Ray Free Electron laser

---

[1] *Picosecond and femtosecond X-ray absorption spectroscopy of molecular systems* M. Chergui, Acta Crystallografica A66 (2010) 229-239

[2] *Femtosecond XANES Study of the light-induced spin crossover dynamics in an Iron(II)-complex*
[2] *Femtosecond XANES Study of the light-induced spin crossover dynamics in an Iron(II)-complex* Ch. Bressler, C. J. Milne, V.T. Pham, A. El Nahhas, R. M. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D.
Ch. Bressler, C. J. Milne, V.T. Pham, A. El Nahhas, R. M. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D. Grolimund, M. Kaiser, C. N. Borca, G. Ingold, R. Abela and M. Chergui, Science 323 (2009) 489-492

[3] *Vibrational relaxation and intersystem crossing of binuclear metal complexes in solution,* R. M. van der Veen, A. Cannizzo, F. van Mourik, A. Vlcek and M. Chergui, Journal of the American Chemical Society 133 (2011) 305-315

[4] *Molecular structural dynamics probed by ultrafast X-ray absorption spectroscopy*, Ch. Bressler and M. Chergui, Annual Review of Physical Chemistry 61 (2010) 263-282

[5] *Probing the transition from hydrophilic to hydrophobic solvation with atomic scale resolution* V.-T. Pham, T. J. Penfold, R. M. van der Veen, F. A. Lima, A. El Nahhas, S. Johnson, P. Beaud, R. Abela, C. Bressler, C. Milne and M. Chergui, Journal of the American Chemical Society 133 (2011) 12740–12748

From Specific Ion Effects to New Ionic Liquids

KUNZ, Werner
Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany

In the last years significant progress has been made in the field of specific ion effects. We are not far from understanding the Hofmeister series and related phenomena. I will briefly review the present state of art.

The understanding of specific ion effects is relevant in many fields, for example to explain the interactions of charged headgroups of amphiphiles with ions in colloidal chemistry and biology, but also to understand the behaviour of Ionic Liquids, i.e. salts with low melting points below 100°C. In the second part of my talk I will report on several new types of Ionic Liquids, for example one that has a simple sodium ion as cation and others which are even edible. Currently, we are also trying to use our knowledge to make ionic surfactants that are liquid at room temperature, i.e amphiphilic Ionic Liquids. I will also make some statements about my point of view concerning the very (too?) fashionable research area of Ionic Liquids.

Some references:

Werner Kunz, Specific Ion Effects, *Current Opinion of Colloid and Interface Science* 15 (2010) 34-39.

Nina Vlachy, Barbara Jagoda-Cwiklik, Robert Vácha, Didier Touraud, Pavel Jungwirth, and Werner Kunz, Hofmeister series and specific interaction of charged headgroups with aqueous ions, *Advances in Colloid and Surface Science* 146 (2009) 42-47.

Oliver Zech, Matthias Kellermeier, Stefan Thomaier, Eva Maurer, Regina Klein, Christian Schreiner, and W. Kunz, Alkali oligoether carboxylates – a new class of ionic liquids, *Chemistry - A European* Journal 15 (2009) 1341-1345

Oliver Zech, Johannes Hunger, Joshua R. Sangoro, Ciprian Iacob, Friedrich Kremer, Werner Kunz, and Richard Buchner, Correlation Between Polarity Parameters and Dielectric Properties of [Na][TOTO] – a Sodium Ionic Liquid, *Physical Chemistry Chemical Physics* 12 (2010) 14341–14350.

Oliver Zech, Pierre Bauduin, Peter Palatzky, Didier Touraud, and Werner Kunz, Biodiesel, a sustainable oil, in high temperature stable microemulsions containing a room temperature ionic liquid as polar phase, *Energy and Environmental Research* 3 (2010) 846-851.

Oliver Zech, Stefan Thomaier, Agnes Kolodziejski, Didier Touraud, Isabelle Grillo, and W. Kunz , Ionic Liquids in Microemulsions - a Concept to Extend the Conventional Thermal Stability Range of Microemulsions, *Chemistry - A European Journal* 16 (2010) 783-786.

Regina Klein, Helen Dutton, Olivier Diat, Gordon J. T. Tiddy,and Werner Kunz, Thermotropic Phase Behavior of Choline Soaps, *The Journal of Physical Chemistry B* 115 (2011) 3838–3847.

Regina Klein, Oliver Zech, Eva Maurer, Matthias Kellermeier, and Werner Kunz, Oligoether Carboxylates – Task Specific Room-Temperature Ionic Liquids, *The Journal of Physical Chemistry B* 115 (2011) 8961–8969.

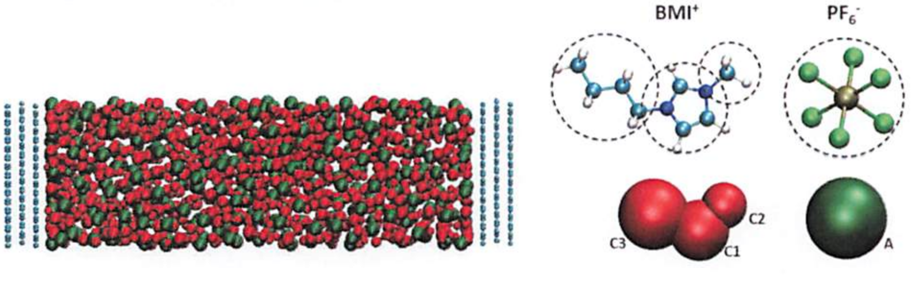
Oliver Zech and Werner Kunz, Conditions for and characteristics of nonaqueous micellar solutions and microemulsions with ionic liquids, *Soft Matter* 7 (2011) 5507–5513.

Modeling Ionic Liquids

MADDEN, Paul
University of Oxford, Materials Department, Parks Road, Oxford OX1 3PH, UK

Modeling can play two generic roles in liquid state and solution chemistry. It may be used to enhance the quality of information emerging from experimental studies by providing insight into the molecular behaviour which underlies observed phenomena. It may also be used to provide values for key data where experiments are not possible – for example, under extreme physical conditions or for highly corrosive materials. In both roles a simulation model which incorporates all the key physical factors is needed but without the computational cost becoming too high to prevent studies on the scale necessary to recapture the phenomena of interest. In the latter role, where predictions of properties of real materials are involved, a very accurate representation of the underlying interactions is necessary. A lot of the effort involves the validation of the simulation model by comparing its predictions with the experimental data which is available, before turning to study the information which is not extractable from experiment alone.

These principles will be illustrated by studies of ionic liquids, both inorganic molten salts and "room temperature" ionic liquids (RTILs) and their mixtures. In the former, where experiments are often difficult, a good deal of work has been done to build accurate, transferable models of the interionic interactions to enable accurate predictions of physical properties. Attention has focused on the role of polarization effects and the use of condensed-phase *ab initio* electronic structure methods to parameterize the interactions on a non-empirical, predictive basis. Molten salts lack the complications introduced by the intramolecular structure of the RTILs, which facilitates the model building and also the validation step by comparison of the predicted structures with diffraction experiments. Nevertheless, the liquids may be quite complex [2], especially the mixtures, because of the formation of coordination complexes and their tendency to link to form networks. These tendencies influence the values of key thermodynamic properties and transport coefficients. Studies of the solvation free energies of different ions [3] in molten salt "solvents", which influence their electrochemical extractability, and of such transport coefficients as the thermal conductivity, which is difficult to measure at high temperature, exemplify the general principles.



RTILs are more difficult to simulate accurately because of the complications of the intramolecular structure; this also means that it is difficult to really home in on *inter*molecular structure in diffraction studies. They also tend to be quite viscous at the temperatures of relevance, which means that long simulations are required to recapture the properties of interest. There is therefore an interest in the development of simplified models, through the use of scaled charges to mimic polarization effects or the use of coarse-grained representations of structural units. An example of the latter is illustrated [4]; the computational simplicity of this representation allows the large-scale study of the properties of an RTIL at a solid interface – important from an electrochemical perspective and also because of the current interest in supercapacitors. When a more accurate, atomic scale representation of the interactions are necessary to recapture chemical effects, a selective inclusion of polarization effects may be the answer. For example, the speciation of the Al-Cl polyions in mixtures of BMICl with $AlCl_3$ is reproduced by allowing only the Cl^- ions to be polarizable in an atomistic model.

1) *Madden et al;* J. Mol. Struct. THEOCHEM 771, 9 (2006).
2) *Salanne et al; J. Phys. Chem.* B, **110**:11461–11467, (2006).
3) *Salanne et al; J. Phys. Chem.* B, **112**: 1177-1183 (2008).
4) *Merlet et al; J. Phys. Chem.* C – to be published
5) *Salanne et al;* RSC Faraday Discussion 154 (2011).

Diffusion-reaction in micro- and nano-confined spaces

AMATORE, Christian
Ecole Normale Supérieure. Département de Chimie. UMR CNRS 8640
24 rue Lhomond. F-75231 Paris Cedex 05. France

Present advances in chemistry and technology allow synthesis of micro- and nanostructures with various properties introduced by the confined environments that can be created. The same exists in nature through specific minerals or has been developed by evolution in living cells.
In chemistry or in biology, the main focus is put on the "chemical" or "biological" properties of such micro- and nanostructures while forgetting that they act in truth as micro- and nano-reactors which must be fed by the desired reactants while the reaction products must be eliminated. In contradiction with normal reactors where chemical engineering is known to be of the utmost importance because transport properties are essential in controlling the reaction fluxes, these fundamental aspects are fully neglected. However, the situation is even more critical for micro- and nanostructures because of the decrease in scales.

It is then of the utmost importance to simultaneously provide conceptual and experimental means for the experimental investigation of micro- and nano-systems which includes not only the very "chemical act" but also the dynamics of transport in micro- and nano-confined environments. This will open entirely new views for the optimization of (bio)chemical reactivity at such level which will serve as a basis for useful innovative nanoscopic devices and advances in biochemical and medical applications such as nanoparticle vectorization of drugs.

This lecture will present discuss several examples of such approaches based on recent works from our team.

Structure and Dynamics of Liquids and Solutions in Confinement

YAMAGUCHI, Toshio
Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814-0180, Japan
e-mail: yamaguch@fukuoka-u.ac.jp

Liquid and solutions in confinement play a vital role in various fields: in separation science like chromatography, in geology such as swelling of clay minerals, in biology of water and ion channels, and in nanoscience and nanotechnology where confined water and solutions contribute to the development of nano-devices and fuel cells, and in pharmaceutical science like drug delivery systems. Thus, the structure and dynamic properties of liquids and solutions in confinement have recently drawn much attention since they are essential for understanding unique properties not available in bulk and underlying mechanisms of chemical processes in confined systems. The unique properties of confined liquids and solutions originate from the interaction between solvent molecules and ions and pore walls and from confined geometry of channels and cage with different pore sizes. This talk reviews the structure and dynamic properties of liquids (mostly water) and ionic solutions in various porous materials measured by FTIR, X-ray and neutron diffraction with EPSR modelling and inelastic neutron scattering (quasi-elastic and spin echo methods). The adsorption/desorption and differential scanning calorimetry measurements were also made to characterize the pores and thermal behaviors of confined liquid and solutions. Various porous materials were employed so that the pore surface varied from hydrophilic to hydrophobic nature; MCM-41 with hydrophilic surface, periodic mesoporous organosilica PMO with hydrophilic and hydrophobic hybrid surface composed of inorganic silica framework embedded by organic groups (phenyl group), and ordered mesoporous carbon OMC and activated carbon fiver with hydrophobic nature. Interesting examples would also be presented for formation of silver metal clusters and ionic liquids in mesoporous MCM-41.

References

T. Yamaguchi, H. Hashi, S. Kittaka, *J. Mol. Liq.* **129**, 57-62 (2006).

S. Kittaka, S. Ishimaru, M. Kurahashi, T. Matsuda, T. Yamaguchi, *Phys. Chem. Chem. Phys.* **8**, 3223-3231 (2006).

T. Yamaguchi, K. Yoshida, P. Smirnov, T. Takamuku, S. Kittaka, S. Takahara, Y. Kuroda, M.-C. Bellissent-Funel, *Eur. Phys. J. Special Topics* **141**, 19-27 (2007).

K. Yoshida, T. Yamaguchi, S. Kittaka, M.-C. Bellissent-Funel, P. Fouquet, *J. Chem. Phys.* **129**, 054702-1-11 (2008).

S. Kittaka, K. Sou, T. Yamaguchi, K. Tozaki, *Phys. Chem. Chem. Phys.* **11**, 8538-8545 (2009).

T. Yamaguchi, H. Sugino, K. Ito, K. Yoshida, S. Kittaka, *J. Mol. Liq.* Available online 12 June 2011.

K. Yoshida, T. Yamaguchi, S. Kittaka, M.-C. Bellissent-Funel, P. Fouquet, *J. Phys. C: Condens. Matt.*
2011, in press.

Oral presentations and keynote lectures Abstracts

Water structure enhancement in water-rich mixtures with organic solvents

MARCUS, Yizhak (Hebrew University)

Liquid water may be described in terms of a two-structure model: a bulky one with nearly 4 hydrogen bonds and a close-packed one with few hydrogen bonds. A clear indication that the bulky, low-density structure of the water is enhanced in water- rich mixtures with co-solvents is the excess partial molar volume of water if it is positive. A similar indication of the enhancement of the water structure is obtained from the excess partial molar heat capacity of the water in such mixtures. This was demonstrated in the cases of aqueous methanol, ethanol, 1-propanol, 2-propamol, t-butanol, diethanolamine, triethanolamine, 1,2-diaminopropane, dimethoxy- ethane, dimethyl-formamide, dimethylacetamide, 2-pyrrolidinone, N-methyl-2-pyrro-lidinone, and dimethylsulfoxide. Some co-solvents that hydrogen-bond very strongly with water, such as ethylene glycol, glycerol, and formamide, do not enhance the water structure according to these criteria. The results are rationalized in terms of the sizes, hydrophobic interactions, and hydrogen bonding properties of the co-solvent molecules.

Spatial decomposition analysis of protein thermodynamics based on the 3D-RISM theory

YAMAZAKI, Takeshi (National Institute for Nanotechnology); KOVALENKO, Andriy (National Institute for Nanotechnology, and University of Alberta, Canada)

We propose the method of spatial decomposition analysis (SDA) based on three- dimensional reference interaction site model (3D-RISM) theory of molecular liquids to study and decompose the thermodynamics of proteins in solution into atomic level contributions. The 3D-RISM theory maps the solvation thermodynamic properties, such as the solvation free energy and solvation entropy, onto the 3D space around the solute, including the excluded volume of the solute macromolecule, with the elementary volume contributions expressed in terms of the 3D total and direct correlation functions. The SDA thus breaks down the thermodynamic quantity into partial contributions of the solute fragments (functional groups or residues) by applying the proximity criterion to the 3D-RISM mapping onto both the solvation shell outside the solute macromolecule and its excluded volume inside the van der Waals cores. This is distinct from the previous use of the proximity criterion applied to the 3D distribution functions in the solvation shell only. For illustration, we apply SDA to four miniproteins composed of 10-28 amino acid residues and decompose their solvation free energy into the partial contributions of each residue. The present results show that SDA is capable of detecting a change in the protein thermodynamics due to mutations and local conformational changes. Furthermore, the SDA exhibits a convincing consistency with the experimental values of the whole-residue transfer free energies from water to octanol. Thus, the SDA provides a meaningful decomposition of the protein thermodynamics which can bear a comparison with experimental measurements and therefore can serve as a valuable sensitive tool to analyze the protein thermodynamics at the atomistic resolution level. In the presentation, we will also discuss about the SDA result of temperature and pressure effects on the protein thermodynamics which can provide us with the implication of temperature and pressure denaturation of protein.

[1] Yamazaki, T.; Kovalenko, A. J. Chem. Theory Comput. 2009, 5, 1723–1730. [2] Yamazaki, T.; Kovalenko, A. J. Phys. Chem. B, 2011, 115, 310–318.

Kinetics and Thermodynamics of Cd(II) Ions Sorption on Mixed Sorbents Prepared from Olive Stone and Date Pit from Aqueous Solution

LOUHAB, Krim (UNIVERSITE)

The removal of toxic metals from wastewater is matter of great interest in the field of water pollution, which is a serious cause of environmental degradation. Besides the classical waste-water treatments, biosorption of heavy metals is an alternative technique, primarily because it utilizes inactive dead biological materials as sorbents which are generally available at low cost, non hazardous and abound in nature. In the last years, certain raw waste products from industrial or agricultural operations i.e. pine bark, grape stalks, crop milling waste have been tested for decontamination of metal-containing effluents.

Date pits constitute roughly 10% of the date palm. In Algeria, which is the largest date pits producer in the world, more than a million ton of date pits are estimated to be generated annually. Date pits as a waste stream is a problem to the date industry, therefore, its recycling or re-use is useful. In the United States, pulverised ground date pits are being used on a small scale, on dirt roads as a type of road base gravel. In the Middle East, it is sometimes used in animal feed. Therefore, finding ways to use this agricultural by-product profitably will benefit date farmers substantially and offers an interesting alternative for their disposal. The olive stone has some applications. Such as combustible, natural fertilizer or additive in animal nutrition. Nevertheless, most of the recent studies have been devoted to the preparation of activated carbon from different olive stone waste and date pit waste. Although the obtained activated carbon by olive stone waste and date pit waste has been reported to be a suitable sorbent material, the cost of the treatment to get the activated carbon makes this sorbent not competitive from the economical point of view[13] would be very interesting to be find out an application to reuse the mixture of olive stone waste and date pits in their native form. In this paper, experiments have been carried out to study the sorption of cadmium ion from aqueous solution using the mixture of olive stone waste and date pits waste. The factors studied include the influence of initial cadmium ion concentration, percentage of olive stone waste and date pits waste in the mixture and temperature on the sorption capacity. A Langmuir model was developed and used to analyse the data for the sorption of cadmium ions by mixture of olive stone waste and date pits. The sorption kinetics may be described as being pseudo-second-order

The aim of this study is to remove Cd(II) ions from aqueous solutions by adsorption. Mixed sorbent prepared from olive stone and date pit, an agricultural solid by- product was used as adsorbent. The adsorption experiments of Cd(II) onto the mixture of olive stone and date pit were conducted at different parameters such as, percent of olive stone and date pit in the mixture, temperature, initial solution pH and initial Cd(II) concentration. Adsorption isotherms were obtained at different percent of olive stone and date pit in the mixture. This adsorption data was fitted with the Langmuir. Kinetic studies revealed that the initial uptake was rapid and equilibrium was established in 20 min for all the studied metals and that the data followed thepseudo-second order reaction. The thermodynamic of Cadmium sorption on the mixed sorbent follows the Langmuir model and the sorption capacity for cadmium increases when we add a small amount of olive stone at date pits (90% of date pits in mixture and 10% of olive stone) and a small amount of date pits at olive stone (90% of olive stone and 10% of date pits in mixture. In addition, the thermodynamic parameters, standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of the adsorption process were calculated. The sorption of Cd(II) onto the mixture of olive stones and dates pit is spontaneous and presents an endothermic nature. The characteristics of the mixture were determined by the analysis of infra red spectral analysis. The results show that the mixture sorbent from olive stone and date pit is an alternative low-cost adsorbent for removing Cd(II).

Possibilities of differential scanning calorimetry method to identify carbon nanomaterials

AVRAMENKO, Natalia (Department of Chemistry Moscow State University; KOROBOV, Mikhail (Department of Chemistry Moscow State University; IVANOVA, Nina (Department of Chemistry Moscow State University ; PARFENOVA, Aksana (Department of Chemistry Moscow State University;SENYAVIN, Vladimir (Department of Chemistry Moscow State University; BELJAEVA, Lubov (Department of Chemistry Moscow State University)

The aim of this research is to develop methods for: 1) obtaining information about the form and structure of pastes and dry nanodiamond powders of detonation synthesis (NDDS); 2) differentiation between pastes and dry samples of aggregated and non- aggregated NDDS. 11 types of nanodiamond samples of various production were studied with DSC method. Two dispersions disaggregated by two different techniques consisted of 4 - 5 and 5 – 15 nm particles. The rest are typical aggregated NDDS which differ in degree of purification and cluster sizes (from 100 to 10000 nm). Pastes were prepared either by non-complete vaporization of original dispersions or by adding a small amount of liquid to a dry sample. DSC method (Mettler DSC-30 scan rate 5 K/min) was used to determine T melting decrease of nanophase compared with bulk material and T melting of bulk water and nanophase of water. Pastes drying (at 800oC heating) recurring addition of water and powder pressing did not effect the position of nanophase melting peak on DSC curves. For the rest of commercial samples nanophase melting peak was not observed. Consequently, it is a successfully reproducible peculiarity for materials made of isolated original nanodiamonds. Nanophase volume of water (0,43 - 0,48 cm3/g), typical size of water nanophase (4,7 - 5,2 nm) as well as mass of water taking part and not taking in melting but forming an adsorption layer (0,9 - 1,0 nm) on the surface of nanodiamond were calculated. Nanophase sizes in nanodiamond - organic liquid (benzene, heptane, cyclohexane, chlorobenzene) were studied by DSC method. The comparison of DSC and nitrogen-adsorption methods demonstrated that DSC method making it possible to investigate nanomaterial layers with various liquids requires less time and material (~2 mg) while the adsorption method allows to obtain pore distribution by sizes. As a result a supposition was made that the paste is a stable secondary structure characterized by a narrow distribution of pores by their sizes and by their constant total volume. Paste structure parameters and its dry powder are the same. Nanoparticles size is less than pore size. Total pore volume in the secondary structure is 0,45 - 0,55 cm3/g. Besides DSC method it was confirmed by isopiestic and sorption methods. The secondary structure can be destroyed by ultrasound influence and therefore a dispersion consisting of primary separate particles can again be obtained. Stable formation of secondary structure could be connected with electrostatic interaction between nanodiamond crystal facets leading to optimal orientation of particular nanocrystals in space.

This work was supported by grant RFBR 09-03-00004

The formation of supramolecular structures in organic solvents

GREENWALD, Iosif (Nizhny Novgorod State Technical University) KALAGAEV, Ivan (Nizhny Novgorod State Technical University)

This experimental data allow to conclude that the strong intermolecular interactions may appear in liquid phase not only for polar, but also for nonpolar solvents. Such interactions may provide the structure of organic solvents even in the absence of classical hydrogen bonds.

The traditional approach to the problem of intermolecular interaction in homogeneous organic liquids includes the consideration of relatively weak van-der-Waals or dispersion forces. In some cases in solvents hydrogen, halogen-halogen or other bonds connected with charge transfer occur. It is well known that some new absorption bands appear in IR spectra of organic compounds at the transaction from gas to liquid state. This concerns medium as well as high frequency region. It is obvious that these bands can be connected with the intermolecular interactions appearing in the condensed state. The comparison data of FTIR spectra analysis in 2400-1400 and 4500-2800 cm-1 regions of a number of the often used in preparative practice organic solvents such as the halogen substituted methanes CX3H (X = Cl, Br), CH2X2 (X = Cl, Br, I), functional methane derivatives CH3X (X = NO2, CN, I), benzene and its derivatives C6H5X (X = H, Cl, Br, NO2), aliphatic hydrocarbons C6H10, C7H16, C8H18 and their deuterated analogs were presented in our work. The revealed in liquid phase bands shift at deuteration of investigated compounds. The isotopic shifts (vH/vD=1.25-1.36) are in good agreement with the theoretical values for harmonic oscillator. This results prove that the observed bands assign to fundamental modes of hydrogen atoms but not to overtones or combination bands. The 2400-1400 cm-1 region is typical for the motion of bounded proton. Since the location of the mentioned bands correlates with the halogen nature (in case of halogen derivatives), it can be assigned to the stretching of intermolecular hydrogen bonds, existing between mobile hydrogen atom and halogen atom of neighboring molecules. The bands in high frequency region (4500-2800 cm-1) may be assigned to modes of dihydrogen bonds analogically to H-H stretching in hydrogen molecule. In the case of aromatic systems we suppose the formation of intermolecular π-hydrogen bonds. This assignment is verified not only by the isotopic shift of the described bands, but also by the expected splitting of bands in substituted benzenes due to non-equivalence of hydrogen atoms in benzene derivatives. In the spectra of organic solvents such as aliphatic hydrocarbons the broad multicomponent band in the 4500-3800 cm-1 region, having the expected isotopic shift (vH/vD=1.29-1.31), is observed. The location of this band and its sensitivity to deuteration indicates the dihydrogen bond formation.

Synthesis and Characterization of Three Novel Resins

FALLAHI, Afsoon (amirkabir university of technology) ; AFSHAR TAROMI, Faramarz (amirkabir university of technology) ; RAJABI, Laleh (Razi University)

In this research, three aromatic Bismaleimide resins, 4,4'-bismaleimidodiphenyl methane (BMIDDM), 4,4'-bismaleimidodiphenylether (BMIDDE) and 4,4'-bismaleimidodiphenyl sulfone (BMIDDS) having various bridging groups from the corresponding amine monomers (4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenylether (DDE) and 4,4′-diaminodiphenylether (DDS)) are prepared respectively in the first part. These resins are synthesized and characterized by IR and NMR spectroscopy techniques. The following part investigates the preparation of BMIDDM/BMIDDE and BMIDDM/BMIDDS mixtures containing various concentrations. This article emphasizes on bismaleimide resin eutectic mixtures. Differential scanning calorimetry analysis of eutectic mixtures of three bismaleimides (4,4′-bismaleimidodiphenyl methane(BMIDDM), 4,4′-bismaleimidodiphenyl ether(BMIDDE) and 4,4′-bismaleimidodiphenyl sulfone (BMIDDS)) that are mixed in different proportions, is used to demonstrate the phase diagrams, the melting and solubility of each constituent of these binary systems via the different liquid and solid phases. Furthermore, in the present paper the relationship between binary systems and the concept of a eutectic mixture with its extraordinary thermal properties is investigated. This study highlights the results of differential scanning calorimetry of the prepared mixtures, as well as initial monomers. The eutectic melting point of the BMIDDM/BMIDDS system is considerable because of its much lower melting point than that of the synthesized monomer with the lowest melting point and also very easy way of using these materials in the molten state. The same DSC thermal study on other mixtures, BMIDDM/BMIDDE and BMIDDE/BMIDDS, is done and the results are reported. The consequences illustrate that the addition of increasing quantities of one monomer to the mixture will result in the appearance of two melting points until getting to the melting temperature of the eutectic composition (Te, a single and homogeneous signal). The same effect of impurities on To and Texo can also be attained. The findings of this work, can be applicable for the transportation industry, particularly in such areas as civil and military aircraft industry, aerospace and in the marine and automotive sectors.

Time-Resolved Translational Diffusion Reveals Kinetics of Reaction Intermediates of Biological Proteins

TERAZIMA, Masahide (Kyoto University)

The translational diffusion processes have been playing very important roles to reveal the nature of molecules or the state of substances in solution. Because of the importance, a variety of techniques to measure the diffusion coefficient have been developed and a number of valuable data have been accumulated. On the other hand, contrary to the well-developed time-resolved spectroscopies, a difficulty we encounter in studying chemical reactions in solution is the fact that the diffusion properties are not easily accessible for transient species. Our group has been working on the time-resolved studies of transport properties during a variety of photophysical and photochemical processes. Here I will report the time-resolved diffusion measurements of some biological proteins performed in our group. We used the pulsed laser induced transient grating and transient lens methods for quantitative measurements of the diffusion change during a photochemical reaction in time domain. We applied this technique to the photochemical reactions of various proteins. Here we will show studies on conformational change of a PixD protein. Most organisms possess photoreceptors that adequately sense and adapt to light environments to allow their survival. The sensors of blue light using FAD (BLUF) are a photoreceptor domain found in many species. PixD proteins are ones of photosensors containing the BLUF domain, and identified in cyanobacteria. Crystallographic analyses showed that these homologous PixD proteins have a unique oligomeric structure: a decamer comprised of two stacked pentameric rings. Because oligomer formation of PixD proteins is also observed in solution, PixD may function as an oligomer in cyanobacterial cells. We found that the decameric form of TePixD can undergo a conformational change that is dependent on the oligomeric state. However, the reason why PixD exists in the decamer form was unknown. We discovered a peculiar dependence of the conformational change of the TePixD decamer on the intensity of the excitation light, which could be related to the importance of the oligomeric form. This study emphasizes that the time-resolved technique of the diffusion process in solution can be used for photochemical reaction in general to investigate the conformational change and the hydrophobic interaction in time domain

Study of Chain Length Effect on Dielectric Relaxation and Thermodynamic Properties of Polymers Using TDR Method

SARODE, Arvind (SWAMI RAMANAND TEERTH MARATHWADA UNIVERSITY,NANDED-431606) ; KUMBHARKHANE, Ashok (SWAMI RAMANAND TEERTH MARATHWADA UNIVERSITY,NANDED-431606)

Temperature and chain length dependence of dielectric relaxation and thermodynamic energy parameters of low molecular weight polypropylene glycols HO[CH(CH3)CH2O)nH with number average molecular weight 425(n=7), 1000 (n=17) and 2000 (n=34) gmol-1 and Poly(ethylene glycols) HO[CH2-CH2-O]nH with number average molecular weight 200 (n=4), 300 (n=7), 400 (n=9) and 600 (n=14)gmol-1 have been studied using Time Domain Reflectometry (TDR) in the frequency region 10MHz-10GHz and in the temperature region 250C-00C. The frequency dependence of the complex dielectric permittivity is analyzed by the Havriliak-Negami expression. The static dielectric constant , high frequency limiting dielectric constant , relaxation time and thermodynamic energy parameters such as free energy, enthalpy of activation and entropy of activation have been determined. The average free energy of activation for PPG-425,PPG-100,PPG-2000,PEG-200 and PEG-300 gmol-1 molecules was found to be in the range 4~5 Kcalmol-1 where as for PEG 400 it was found in the range 3.5 ~ 4.0 Kcalmol-1. For PEG-600 there observed a large variation in the value of from 2.43 to 4.32 Kcalmol-1 . This variation in the value of free energy of activation for PEG-600 may be due to change in the structural properties when studied below its freezing point. The values of entropy for PPG-2000 molecules were found to be negative while entropy for PPG-425 and PPG-1000 molecules found positive, which confirms that the configuration of PPG-2000 involved in the dipolar orientation has an activated state, which is more ordered than in the normal state compared to PPG-425 and PPG-1000 molecules. Similar results have been observed for poly(ethylene) glycol molecules. Keywords: Poly(Propylene Glycol);Poly(ethylene glycol) ; Time Domain Reflectometry(TDR);Dielectric Relaxation; Thermodynamic Parameters. PACS Nos: 77.22 (GM)

A transferable model of water

BARANYAI, András (Institute of Chemistry, Eötvös University

The two most frequently used models of water, TIP3P and SPC/E, form false geometries of gas phase clusters.1 We have shown that this problematic behavior is also present in their many-body structure of ambient liquid water.2 For correct results the position of the negative charge for classical models should be shifted from the oxygen atom towards the hydrogen atoms.2 We developed a new model for the water molecule3 which contains only three Gaussian charges. Using the gas phase geometry, the dipole moment of the molecule matches, the quadrupole moment closely approximates the experimental values. The negative charge is connected by a harmonic spring to its gas-phase position. The polarized state is identified by the equality of the intermolecular electrostatic force and the spring force acting on the negative charge. In each timestep the instantaneous position of the massless negative charge is determined by iteration. Using the technique of Ewald summation, we derived expressions for the potential energy, the forces, and the pressure for Gaussian charges.3 Our model is capable to provide good estimate for the properties of gas clusters, ambient water, hexagonal ice, ice III, ice VI, and several ice VII phases.3,4 The high-pressure phases are modeled by using two simple exponentials with r-6 attractions and a switch function. One of the exponentials represents the repulsion under low pressure, the other is the repulsion under high pressure. The switch function varies between 0 and 1 and portions the two repulsions among the individual particles. The argument of the switch function is a virial-type net force acting on the molecule.4 [1] P.T. Kiss and A. Baranyai, J. Chem. Phys., 131, 204310 (2009) [2] P.T. Kiss and A. Baranyai, J. Chem. Phys., 134, 054106 (2011) [3] A.Baranyai and P.T. Kiss, J. Chem. Phys., 133, 144109 (2010) [4] P.T. Kiss and A. Baranyai, J. Chem. Phys., submitted

Measurement of the pure dissolution rate constant of a soft mineral in water

COLOMBANI, Jean (Université Claude Bernard Lyon 1) PACHON-RODRIGUEZ, Alejandro (Université Claude Bernard Lyon 1)

In standard dissolution experiments (rotating disk, batch, ...), the mineral dissolves in stirred water. So the dissolution kinetics is blurred by diffusive and most of all convective contributions. For hard minerals, dissolution is so slow that it drives the whole kinetics and convection can be forgotten. For softer minerals dissolution, diffusion and convection timescales are of the same order of magnitude and are difficult to distinguish. We have collected all the dissolution rates of gypsum in water measured by various methods found in the literature. No coherence exists between them and the deduced dissolution rate constants span over several decades. Therefore we have analysed the hydrodynamics of all the devices, removed the convective contribution and deduced from them the pure surface reaction rate constant of gypsum in water. It appears to be much smaller than expected from the literature results. An holographic interferometry experiment, performed in still water, is carried out and enables to measure directly this rate constant. Both values agree within experimental uncertainty.

Multiscale modeling of solvation in chemical and biological nanosystems and nanoporous materials

KOVALENKO, Andriy (National Institute for Nanotechnology)

A challenge of multiscale theory, modeling, and simulation of nanosystems Nanoscale properties, phenomena, and processes are profoundly different from the macroscopic laws governing the behaviour of continuous media and materials. Functional features of nanostructures all stem from microscopic properties of the atoms and chemical groups they are built of, but manifest on length scale from one to hundreds nanometers and time scale up to microseconds and more. By changing size, composition, and fabrication protocol, the properties of nanostructures and processes involving them can be tuned up in a wide range. Predictive modeling of nanosystems should operate at length scales from an Angström to hundreds nanometers and time scales to microseconds and more, and yet derive their properties from the chemical functionalities of the constituents. Explicit molecular modeling of such nanosystems involves millions and billions of molecules and is by far not feasible in a "brute force" approach employing just ab initio quantum chemical methods and/or molecular simulations. A proper way thus requires multiscale methods coupling several levels of description, from electronic structure methods for building blocks and classical molecular simulations for critical aggregates in the system, to statistical-mechanical theories for their large assemblies and mean properties in a statistical ensemble over characteristic size and time scales, to eventually come up with macroscopic scale properties of the nanostructures and related processes showing up in the "real observable world". A true, genuine challenge of multiscale modeling is a theoretical framework that couples methods at different scales, so that observables at lower-level scales are analytically linked to force fields of more coarse-grained models at higher-level scales. Statistical mechanics itself is an example of

such a theoretical coupling between microscopic molecular variables and thermodynamic, macroscopic properties.

Multiscale, self-consistent field coupling of 3D-RISM-KH molecular theory of solvation with electronic structure theory and molecular dynamics simulation for modeling of chemical and biological systems

The statistical-mechanical, molecular theory of solvation, also known as three- dimensional reference interaction site model (3D-RISM), starts from an explicit solvent model with all-atom force field but operates with 3D correlation functions of species in a statistical ensemble rather than with individual molecular trajectories and predicts the solvation structure and thermodynamics from the first principles of statistical mechanics [1]. Complemented with the Kovalenko-Hirata (KH) closure approximation [1,2], the 3D-RISM integral equation theory properly accounts for chemical specificities of solute and solvent molecules or macromolecules by representing in a single formalism both electrostatic and non-polar features of the solvation structure, such as hydrogen bonding, hydrophobicity, salt bridges, structural solvent, association, ligand binding, electrochemical effects, etc. Moreover, the 3D-RISM-KH theory analytically yields the solvation thermodynamics in terms of the 3D correlation functions, including the solvation free energy, its energetic and entropic decomposition, and partial molar volume effects [1-23]. It also allows one to decompose any solvation thermodynamic property into partial contributions from interaction sites or functional groups of the solute molecule (e.g., ligand or protein), which constitutes a basis of the method of spatial decomposition analysis (SDA) of solvation effects in association of organic supramolecular complexes and proteins in solution [4]. By comparison with molecular dynamics (MD) simulations with explicit solvent, we demonstrated that the 3D-RISM-KH theory accurately predicts the solvation structure of biomolecular systems as large as the GroEL/ES chaperon complex, but yields the results on a drastically reduced computational time [5].

The 3D-RISM-KH molecular theory of solvation revealed the molecular mechanisms of self-assembly and conformational stability of such complex synthetic organic supramolecular nanoarchitectures as rosette nanotubes (RNTs) forming in different solvents and held through noncovalent forces [6-10]. The molecular building block, Cytosine∧Guanine motif decorated with various functional groups, undergoes an hierarchical self-assembly process in solution to form a six-membered supermacrocycle (rosette ring) maintained by 18 hydrogen bonds between its complementary sites, which in turn self-organizes into a linear stack (a nanotube with an open central channel), an aggregate which in general is highly stable and readily withstands boiling and drying. Any functional group covalently attached to the motif, for example, crown ether, alkyl chains, and lysine tails, could be expressed on the RNT surface, thereby offering a general "built-in" strategy for tailoring the physico-chemical properties of RNTs. The 3D-RISM-KH theory uncovered the pathways of step-by-step self-assembly of RNTs from motifs into rosettes and then nanotubes, showing that the thermodynamically preferred mechanism of RNT growth is attachment of motifs to the nanotube end to form and complete a new rosette ring, rather than growth of a separate ring in solution and then its attachment to the nanotube end [9]. The theory exhibited that the RNT channel is covered with a wetting monolayer of structural water molecules strongly bound to its surface and crucially contributing to the RNT stability, holds a chain of loosely bound water molecules at the channel center, and can also hold host molecules of inert gases or drugs inside [9]. This suggests potential use of RNTs as artificial channels for molecular transport in nanoengineered bioorganic systems and as drug delivery vehicles. The 3D-RISM-KH theory predicted that a G∧C base bearing two C12 alkyl chains undergoes a solvent-controlled multistep hierarchical self-assembly process into lamellar prolate nanospheroids [8].

The theory explained how the stability of the helical rosette nanotubes (HRNs) self-assembling from the C∧G motif decorated with the lysine tail can be tuned (significantly increased) by adding a covalent linker pairing adjacent G∧C bases in neighboring rings, and how HRNs undergo further hierarchical self- organization into superhelices [6]. The theory predicted the molecular mechanism of solvent-driven supramolecular chirality in HRNs: structural solvent molecules localized in the pockets between the lysine tails on the HRN surface play a role of molecular switches causing the tails to form a right-hand supramolecular helix in water, the conformation with the lowest free energy (thermodynamic formation), but a left-hand supramolecular helix in methanol, the conformation preferred due to a kinetic barrier for the right-hand one at the beginning of HRN self-assembly in methanol (kinetic formation), but undergoing subsequent conversion to the right-hand one under heating, in full agreement with experiment [7]. The 3D-RISM-KH theory predicted the most stable conformation of the RNTs made of twin G∧C module bearing the lysine side chain, with the "nests" consisting of four side chains used for one-pot nucleation, growth, morphogenesis, and passivation of 1.4 nm Au nanoparticles, one of the possible applications of RNTs [10].

We coupled the 3D-RISM-KH molecular solvation theory with ab initio CASSCF quantum chemical method [1,11] as well as with Kohn-Sham density functional theory (KS-DFT) in a self-consistent field description of electronic structure in solution [1,2,12,13]. This included analytical gradients of the solvation free energy, giving access to optimized geometry, chemical reactions, and nanocatalysis in solution [12,13]. We also coupled 3D-RISM-KH with Wesolowski and Warshel's orbital-free embedded density functional theory (OFE-DFT) based on a two-density functional for electronic structure in an environment, which yields an advanced description of solution environment effects, in particular, photochemistry in solution [14]. We have implemented the (OFE)KS-DFT/3D-RISM-KH multiscale method in the ADF computational chemistry package [12-14], and extensively validated it against experimental data and/or high-level ab initio calculations for solvation structure and thermochemistry, conformational equilibria, and activation barriers of chemical reactions for nanosystems with various solutes (including carbon nanotubes) and solvents [12,13], photochemistry in solution [14], and ionic liquids [15].

The 3D-RISM-KH molecular theory of solvation also replaces the MM/PB(GB)SA post-processing approach involving empirical non-polar terms with the MM/3D-RISM-KH statistical-mechanical evaluation of the solvation thermodynamics [16]. We applied the MM/3D-RISM-KH post-processing method to study the thermodynamics and volumetrics of the hydration and aggregation of the HET-s prion and amyloid-β fibril [17], and the conformational stability and association thermodynamics of small wild-type Aβ(17–42) oligomers with different protonation states of Glu(22) versus the E22Q (Dutch) mutants [16].

Further, we coupled the 3D-RISM-KH theory contracting the solvent degrees of freedom with MD simulation applied just to the solvated biomolecule, and implemented this hybrid method in the Amber molecular dynamics package [18]. The coupling included several accelerating schemes and multi-time steps up to 20 fs to enable simulation of large biomolecules. The method allows one to study biomolecular processes in solution on extremely long timescales, such as aggregation of prion proteins [17], β-sheet Amyloid oligomers [16,17,19], protein-ligand binding [19], and function-related solvation in confined and inner spaces of biomolecular complexes as large as the GroEL chaperon complex [5], and the Gloeobacter violaceus pentameric ligand-gated ion channel (GLIC) in lipid bilayer [20].

The 3D-RISM method offers a new computational approach to molecular recognition in solution, in particular, protein-ligand binding [21]. From the first principles of statistical mechanics, the 3D-RISM integral equation theory allows one to map ligand molecules onto protein surfaces and identify their most probable binding modes through conspicuous peaks in the 3D density distributions of the ligand around protein, with strong potential toward computational fragment-based drug design [22]. Very recently, we have incorporated the 3D-RISM-KH theory into the protein-ligand docking framework implemented in the AutoDock package, to properly account for molecular specificity and composition of species constituting the solution, including solvent, co-solvent, ligand at a finite concentration, and buffer [23]. As a case study, our new 3D-RISM-Dock approach yields 3D maps of binding of the 2-pyrrolidin-1-yl-N-(4-(4-(2-pyrrolidin-1-yl-acetylamino)benzyl)phenyl)acetamide ligand [24] to the mouse prion protein (PrPC) with proper account of molecular specificity of the ligand and solvent, and allows one to study concentration effects on protein-ligand binding in fragment based rational drug design [23].

Molecular theory of solvation and electrical double layer in nanoporous material

The properties of an electric double layer (EDL) formed in inner spaces of nanoporous electrodes are very different from a conventional, planar electrochemical capacitor of equal surface area due to an overlap of adjacent EDLs. The EDL at the surface of carbon nanopores gets substantially distorted, compared to that at a planar electrode in contact with electrolyte solution, resulting in the specific capacitance per surface area by up to 2 orders of magnitude less than for the planar electrode. At present, molecular simulation description of these effects is virtually unfeasible due to the interplay of long-range electrostatic and short-range steric interactions on large-space and long-time scales, and the necessity to satisfy the conditions of chemical and mechanical balance between the species in the bulk electrolyte solution and those sorbed in the nanoporous electrodes. A generalization of RISM molecular theory of solvation to solutions sorbed in disordered nanoporous materials using the replica method for statistical mechanics of quenched-annealed systems, the so-called replica RISM-KH-VM theory, provides full microscopic details of the solvation structure and thermodynamics averaged over the thermal motion of sorbed solution and over the quenched distribution of host nanoporous material (morphology of nanopores) [25-27]. This theory enables predictive molecular modeling of thermochemistry and electrochemistry of electrolyte solutions sorbed in functionalized nanoporous materials. In particular, it reveals the mechanisms of sorption and supercapacitance in nanoporous carbon electrodes [25-32]. The replica RISM-KH-VM theory predicts, from the first principles of statistical mechanics, such effects as solvent-specific wetting [26] and water depletion in hydrophobic carbon nanopores [28-30], asymmetry in solvation and adsorption of cations and anions [27-30], salting-out of simple ions in hydrophobic nanopores and its reversal with external voltage applied [27-31], efficient removal of ionic impurities from an aqueous waste stream by a nanoporous carbon electrosorption cell [29], and specific adsorption at chemical functionalities on the surface of carbon nanopores [25,32].

The RISM-KH-VM theory yields realistic values of the specific capacitance of nanoporous carbon electrodes and reveals that the electrochemical mechanism of the EDL supercapacitor is determined largely by the chemical balance for sorbed ions in the Nernst-Planck equation, rather than just by the EDL potential drop at the surface of a nanopore as in the case of a planar electrode [27-31]. The same molecular forces determine for the specific sorption capacity and purification efficiency of a nanoporous carbon electrosorption cell [29]. The specific capacitance and sorption capacity of nanoporous carbon electrodes are determined by the interplay of the EDL potential drop across the Stern layer at the surface of nanopores and the Gouy- Chapman layer statistically averaged over the volume of the nanoporous material, the osmotic term due to a difference between the ionic concentrations in the two nanoporous electrodes and in the bulk electrolyte solution outside, and the chemical potentials of sorbed solvated ions statistically averaged over the nanoporous material [27-31]. The latter are strongly affected by chemical specificity of ions, solvent, surface functional groups, and steric effects for solvated ions confined in nanopores. The chemical potentials of solvated ions in nanopores constitute a major factor driving the specific capacitance, as they bring about two extra EDLs at the outer boundaries of the nanoporous electrodes to offset the chemical potential difference between the electrodes and solution bulk, and thus substantially contribute to the supercapacitor voltage [27-30]. The RISM-KH-VM theory shows how pseudocapacitance effects in nanoporous carbon impregnated with Co3O4 nanoparticles affect the voltage diagram and specific capacitance of the EDL supercapacitor [32].

References

[1] A. Kovalenko, Three-dimensional RISM theory for molecular liquids and solid- liquid interfaces, in: Molecular Theory of Solvation, F. Hirata (ed.). Series: Understanding Chemical Reactivity, vol.24, (Kluwer, Dordrecht, 2003) pp.169-275. [2] A. Kovalenko and F. Hirata, J. Chem. Phys. 110, 10095 (1999).

[3] Y. Harano, T. Imai, A. Kovalenko, M. Kinoshita, F. Hirata, J. Chem. Phys. 114, 9506 (2001).

[4] T. Yamazaki and A. Kovalenko, J. Chem. Theory Comput. 5, 1723 (2009); J. Phys. Chem. 115, 310 (2011). [5] M. C. Stumpe, N. Blinov, D. Wishart, A. Kovalenko, V. S. Pande, J. Phys. Chem.B 115, 319 (2011); Journal cover.

Content :

[6] J. G. Moralez, J. Raez, T. Yamazaki, R. K. Motkuri, A. Kovalenko, H Fenniri, J. Am. Chem. Soc. 127, 8307 (2005). [7] R. S. Johnson, T. Yamazaki, A. Kovalenko, H. Fenniri, J. Am. Chem. Soc. 129, 5735 (2007).[8] G. Tikhomirov, T. Yamazaki, A. Kovalenko, H. Fenniri, Langmuir 24, 4447 (2007). [9] T. Yamazaki, H. Fenniri, A. Kovalenko, Chem Phys Chem. 11, 361 (2010). [10] R. Chhabra, J. Moralez, J. Raez, T. Yamazaki, J.-Y. Cho, A. Myles, A. Kovalenko, H. Fenniri, J. Am. Chem. Soc. Communication 132, 32 (2010). [11] H. Sato, A. Kovalenko, F. Hirata, J. Chem. Phys. 112, 9463 (2000). [12] S. Gusarov, T. Ziegler, A. Kovalenko, J. Phys. Chem. A 110, 6083 (2006). [13] D. Casanova, S. Gusarov, A. Kovalenko, T. Ziegler, J. Chem. Theory Comput. 3, 458 (2007). [14] J. W. Kaminski, S. Gusarov, T. A. Wesolowski, A. Kovalenko, J. Phys. Chem. A 114, 6082 (2010). [15] M. Malvaldi, S. Bruzzone, C. Chiappe, S. Gusarov, A. Kovalenko, J. Phys. Chem. B 113, 3536 (2009). [16] N. Blinov, L. Dorosh, D. Wishart, A. Kovalenko, Biophys. J. 98, 282 (2010). [17] T. Yamazaki, N. Blinov, D. Wishart, A. Kovalenko, Biophys. J. 95, 4540 (2008). [18] T. Luchko, S. Gusarov, D. R. Roe, C. Simmerling, D. A. Case, J. Tuszynski, A. Kovalenko, J. Chem. Theory Comput. 6, 607 (2010). [19] N. Blinov, L. Dorosh, D. Wishart, A. Kovalenko, invited paper, Molec. Simul. (2011), in press. [20] N. Blinov and A. Kovalenko, invited paper, J. Molec. Liq., (2011), submitted. [21] N. Yoshida, T. Imai, S. Phongphanphanee, A. Kovalenko, F. Hirata, Feature Article, J. Phys. Chem. B 113, 873, (2009). [22] T. Imai, K. Oda, A. Kovalenko, F. Hirata, A. Kidera, J. Am., Chem. Soc. 131, 12430 (2009). [23] D. Nikolic, N. Blinov, D. Wishart, A. Kovalenko, (2011), to be submitted. [24] K. Kuwata, N. Nishida, T. Matsumoto, Y.O. Kamatari, J. Hosokawa-Muto, K. Kodama, H. K. Nakamura, K. Kimura, M. Kawasaki, Y. Takakura, S. Shirabe, J. Takata, Y. Kataoka, S. Katamine, Proc. Natl. Acad. Sci. USA 104, 11921 (2007). [25] A. Kovalenko and F. Hirata, J. Chem. Phys. 115, 8620 (2001). [26] A. Kovalenko and F. Hirata, J. Theor. Comput. Chem. 2, 381 (2002). [27] A. Kovalenko and F. Hirata, Condensed Matter Phys. 4, 643 (2001). [28] A. Tanimura, A. Kovalenko, F. Hirata, Chem. Phys. Lett. 378, 638 (2003). [29] A. Kovalenko, J. Comput. Theor. Nanosci. 1, 398 (2004). [30] A. Tanimura, A. Kovalenko, F. Hirata, Langmuir 23, 1507 (2007). [31] A. Tanimura, A. Kovalenko, F. Hirata, (2011), to be submitted. [32] S. Gusarov, S. Koutcheiko, D. Mitlin, A. Kovalenko, (2011), to be submitted.

Statistical-mechanical, 3D-RISM-KH molecular theory of solvation structure and thermodynamics is an essential part of the multiscale methodology for chemical and biological nanosystems in solution. We coupled 3D-RISM-KH with ab initio CASSCF, Kohn-Sham and orbital-free embedded DFT quantum chemistry methods in a self- consistent field description of electronic and solvation structure, optimized geometry and chemical reactions in solution, and extensively validated this multiscale method against experiment for solvation thermochemistry, photochemistry, conformational equilibria, and activation barriers of various nanosystems in different solvents and ionic liquids. We employed it to explain the molecular mechanisms of self-assembly, conformational stability, and solvent-driven supramolecular chirality of organic rosette nanotubes. We coupled 3D-RISM-KH contracting the solvent with MD simulation treating the solvated biomolecule and implemented that in Amber package, including several accelerating schemes and multi- time steps up to 20 fs. This enables study of extremely slow processes such as aggregation of β-sheet Amyloid oligomers, protein-ligand binding and function- related solvation in confined spaces of biomolecular complexes as large as GroEL chaperon. It replaces MM/PB(GB)SA post-processing involving empirical non-polar terms with MM/3D-RISM-KH statistical-mechanical evaluation of the solvation thermodynamics. Our replica RISM-KH-VM molecular theory for electrochemistry of electrolyte solutions in nanoporous materials reveals the molecular mechanisms of sorption and supercapacitance in nanoporous carbon electrodes, drastically different from a planar electrical double layer.

From Molten Salt to Electrolyte Solution: Dynamics of Ionic Liquids and their Mixtures

BUCHNER, Richard (Universitaet Regensburg, Institut fuer Physikalische und Theoretische Chemie)

Due to their wide range of potential applications room-temperature ionic liquids (RTILs) and their mixtures with polar and non-polar components are intensively investigated and significant progress was made during the last decade. Major aims of these studies are thermodynamic and transport properties but also detailed molecular- level information on the structure has become available from scattering experiments, various spectroscopies and mainly computer simulations. On the other hand, our understanding of molecular motions in RTILs and their mixtures is still rather limited. Major reason for that is the intrinsic complexity of this dynamics which is heterogeneous, highly collective and characterized by strong coupling of translational and rotational contributions. The situation is aggravated by the generally high viscosity of RTILs which complicates many experiments and makes computer simulations of their molecular dynamics cumbersome.

This report summarizes recent results obtained with dielectric spectroscopy on the dynamics of pure RTILs and their mixtures with polar solvents and places them into context with information from other methods. It is shown that in pure RTILs localized molecular motions span from a few tens of femtoseconds for librations of the constituting ions to several nanoseconds for the breathing motions of larger aggregates before steady-state diffusion of the ions is reached. On this timescale translational motions are caged, leading to strong collective intermolecular vibrations. As a consequence individual long-lived ion pairs generally do not exist in pure RTILs but exceptions are possible.

On dilution of the RTIL with a polar component dynamics is accelerated and gets more homogeneous. However, the molten-salt like behavior is kept down to RTIL mole fractions of x_RTIL = 0.2-0.4, depending on the additive. At even lower x_RTIL the mixtures behave as conventional electrolyte solutions. The dielectric spectra show that due to their low surface-charge density most ions constituting RTILs are only weakly solvated in this state. Depending on the polar component and the RTIL a more or less pronounced tendency to form contact ion pairs (CIPs) is observed at x_RTIL < 0.1. These CIPs gradually disappear with increasing RTIL content, possibly through the formation larger aggregates, before the smooth transition from electrolyte- solution to molten-salt-like behavior is occurs.

Mobility of water molecules in ion hydration shells and dielectric spectroscopy data in whole orientation frequency range

LYASHCHENKO, Andrey (Kurnakov Institute of General and Inorganic Chemistry RAS) ;LILEEV, Alexander (2Moscow State University of Environmental Engineering) ; NOVSKOVA, Yamara (1Kurnakov Institute of General and Inorganic Chemistry RAS)

We analyzed the experimental and theoretical aspects of this problem. The mechanism of water molecules dynamics in hydration shells of ions is considered on the basis of confined rotator theoretical model for N fractions of solution water with different types of elementary motions, experimental dielectric (in the range 7-120 GHz) and absorption (up to 800 cm-1) data. The spectra of complex dielectric permittivity and absorption in far IR, submillimeter and microwave regions are described using the theoretical scheme. The particularities of millimeter and submillimeter areas are established. The high frequency boundary of Debye relaxation zone is determined. The differences of ions with positive and "negative" hydration (Samoilov, s approach) or ions "without hydration" (Bernal and Fouler's approach), hydrophilic and hydrophobic hydration are determined at the level of elementary orientation processes. The measurements of high frequency dielectric permittivity and losses were carried out at the frequency range 7-120 or 7-25 GHz and temperatures 283-313 or 288-308 K for 50 binary water-electrolyte systems. They include the aqueous solutions of fluorides, chlorides, nitrates, sulfates, formates, acetates, propionates of alkali metals, ammonium salts and the solutions of tetralkylammonium and tetraallylammonium salts. The low frequency specific conductivity of these solutions was measured for determination of the ionic losses. The relation between the dipole and ionic losses was determined at various concentrations and temperatures up to 150 GHz. Complex dielectric permittivity of the investigated solutions is described by the Debye or Cole-Cole equations. Thus the one most probable relaxation time takes place in this spectral dielectric window. It is related to bulk water and hydration shells of ions. The static dielectric permittivity, activation enthalpy and dielectric relaxation time are calculated for the above mentioned solutions. We present the classification of aqueous electrolytes solutions with different hydration types of cations and anions using dielectric relaxation data in temperature range. New criteria of the difference between the hydrophilic and hydrophobic hydration of ions are suggested. The stabilization of initial water structure (τs>τH2O, ΔHε++s>ΔHε++H2O) in some character cases of hydrophilic hydration (NH4H2PO4, (NH4)3PO4 for example) is established. General relations between dielectric relaxation parameters and structural effects in aqueous salt solutions are considered. The increase in complementary structural organization of water in the bulk and hydration shells of ions leads to the molecular-kinetic stabilization of water and the structure-making effect. Structure breaking effect realizes in the opposite case. It explains the difference between water mobility in initial concentration range for a wide variety of electrolyte solutions.

This work is supported by the grants of Presidium RAS.

Thermodynamic and structural investigation of the trivalent actinides complexation with DTPA

LEGUAY, Sébastien (CNRS. Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex Orsay (groupe radiochimie), France) ; VERCOUTER, Thomas (CEA, DEN, Saclay, F-91191 Gif-sur-Yvette, France) ; TOPIN, Sylvain (CEA, DAM, DIF F-91297, Arpajon, France) ; AUPIAIS, Jean (CEA, DAM, DIF F-91297, Arpajon, France) ; LE NAOUR, Claire (CNRS. Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex Orsay (groupe radiochimie), France) ; MENDES, Mickael (CNRS. Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex Orsay (groupe radiochimie), France) ; MIGUIRDITCHIAN, Manuel (CEA, DEN, Marcoule BP 17171, 30207 Bagnols sur Ceze, France) ; MOISY, Philippe (CEA, DEN, Marcoule BP 17171, 30207 Bagnols sur Ceze, France) ; GUILLAUMONT, Dominique (CEA, DEN, Marcoule BP 17171, 30207 Bagnols sur Ceze, France

Beside uranium and plutonium recovery, reprocessing of spent nuclear fuel requires efficient separation of long-lived actinides (americium, curium) from fission products, especially lanthanides. This is a real challenge since these elements display close chemical properties. Among various separation processes, the TALSPEAK [1] one involves Diethylene Pentaacetic Acid (DTPA) as selective extractant. The affinity of DTPA for trivalent actinides (An(III)) is higher than that for trivalent lanthanides (Ln(III)). Therefore, An(III) are retained in aqueous phase (lactate buffer solution) whereas Ln(III) are extracted into the organic phase by di(2-ethylhexyl)phosphoric acid (HDEHP). About ten studies on the speciation of An(III) in the presence of DTPA have been conducted with the aim of improving the Talspeak process. However, discrepancies in thermodynamic data [2,3] relative to complexation equilibria of An(III) with DTPA do not allow to get a reliable speciation diagram as function of pH and temperature. In the present work, formation constants relative to have been deduced from multitechnique measurements (Time Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS), solvent extraction, UV-visible spectrophotometry and Capillary Electrophoresis coupled with Mass Spectrometer (CE-ICP-MS)). The conditional complexation constants are a function of pH that reveals a slope change. This has been correlated to the existence of protonated and non-protonated complexes: AnHDTPA– and AnDTPA2–. This model also explains previously reported experimental data. Relative constants of AnHnDTPA-2+n complexes for Am(III), Cm(III), and Cf(III) have been determined simultaneously by CE-ICP-MS which shows a greater stability of the DTPA complexes of Cf(III) compared with the two other actinides. The complexes structures have been optimized using the density functional theory (DFT). Distances An-O and An-N have been determined for AnHDTPA– and AnDTPA2– complexes with and without water molecules in the coordination sphere.

Acknowledgements This work was supported by PACEN/GNR PARIS (French Organization).

References: [1] Weaper, B.; Kappelman, F.A. ORNL-3559, August, 1964 [2] Brandau,E.; Inorg. Nucl. Chem. Let., 1971, 7, 1177 [3] Baybarz, R. D. J. Inorg. Nucl Chem., 1965, 27, 1831

Towards a more comprehensive modelling capability for aqueous solution thermodynamics

ROWLAND, Darren (Murdoch University) MAY, Peter (Murdoch University)

The field of electrolyte solution thermodynamics has a long history. Despite decades of research however, no fundamental framework for describing the properties of electrolyte solutions has emerged. Numerous theoretical formulations have been developed which attempt to correlate the physicochemical properties of pure and mixed electrolytes in aqueous solution, but none of these are capable of accurately predicting the thermodynamics of multicomponent electrolyte mixed solutions, such as seawater. The reasons for this lack of consensus are numerous. It is only in very dilute solutions that fundamental electrolyte solution theory is well established. In general, available thermodynamic models are based largely on empirical functions – with correspondingly poor predictive capability. Also, experimental information on mixed electrolyte systems is worryingly sparse and the consequences of error propagation from uncertainties in the raw experimental data and from poorly designed numerical analyses are widely underestimated.

We aim to address this problem by assembling as much relevant information on physicochemical properties as possible into a large, general database and to provide automatic computational methods to analyse the diverse data for thermodynamic consistency. Then, by focussing on the linear mixing rules of Zdanovskii and Young, robust and accurate predictions of the properties of mixed electrolyte solutions can be achieved.

A good model for the water activity of binary solutions is required by Zdanovskii's rule to predict the water activity of mixtures. Likewise, the use of Young's rule needs the density (or heat capacity) of binary solutions. Satisfactory fits to these properties of binary solutions can be obtained using the Pitzer equations. The empirical nature of the Pitzer model is much less problematic for binary solutions than for mixtures. This is because the combinatorial escalation in the number of required parameters is avoided.

This work describes an automatic optimisation procedure for fitting physicochemical data and the subsequent calculation of mixture properties using Zdanovskii's rule and Young's rule. We have found that many systems are very well described using this approach. However, difficulties have been encountered when representing certain properties, in particular trace activity coefficients. Possible ways of dealing with this problem are being investigated.

Formation and testing of honge oil as a biodiesel

PARASHAR, Amit (G.L.bajaj Group of Institutions, Mathura)

Abstract The increasing industrialization and motorization of the world is leading to a steep rise in the demand of petroleum products. The petroleum-based fuels are stored fossil fuels in the earth. There are limited reserves of these fossil fuels. It is feared that they are not going to last long. In this paper, the authors have made an attempt to introduce honge oil, which is blended with diesel in its production and properties (when used in I.C.engine). The performance characteristics compared with conventional (diesel) fuel and their environmental pollution characteristics are also discussed. A single cylinder of Kirloskar make, water-cooled engine, was used in experimental setup.

Generalized excluded volume: its origin and effects

NEZBEDA, Ivo (Inst. Chem. Process Fund., Acad. Sci.) Presenter : NEZBEDA, Ivo (Inst. Chem. Process Fund., Acad. Sci.)

The idea of the existence of an excluded volume (i.e., an impenetrable volume of molecules) formed the basis of the intuitive van der Waals (vdW) equation. After putting this idea on a rigorous statistical mechanical footing, the excluded volume has been used to interpret, or even estimate semi-quantitatively, a number of properties of fluids. All these facts are a consequence of the predominant effect of short-range repulsive forces acting between the molecules. This concept of the ordinary excluded volume however fails for fluids in which, in addition to omnipresent repulsive interactions at short separations, also specific short-range attractive interactions play an important role as, e.g., for associating fluids.

To model associating fluids at a very simple level, we introduced some time ago the so called primitive models which have formed later the basis of nowadays widespread SAFT method. The models mimic, by means of a square-well attraction and hard sphere repulsion, the interactions between the unlike and like interaction sites embodied to molecules, respectively, at short separations. When all attractive interactions are switched off one gets then the so called pseudo-hard body (PHB). These PHB's may be viewed as a counterpart of hard spheres and play the same role for understanding the behavior of associating fluids and developing theory thereof which hard spheres have played for simple fluids.

After a brief introduction of PHB's and their peculiar properties, a number of examples is presented showing that such generalized excluded volumes are able to explain naturally, without any parameter fitting, anomalous properties of aqueous solutions.

Electrophoretic mobility and speciation: experiments, interpretation and problems

AUPIAIS, Jean (CEA)

Recently, the coupling of capillary electrophoresis with an inductively coupled plasma mass spectrometer (ICPMS) found applications to speciation studies, by detecting either several species (if their stabilities are enough strong to not dissociate during the separation run time) or labile species (which corresponds to one average peak because of fast equilibria occuring between all species during the separation run time). Thermodynamical quantities have been successfully derived for several unknown systems but require, in some cases, to arbitrarily set the electrophoretic mobility of the complexes. The mobility of the complexes is assessed according to several rules, e.g. their charges, the limiting electrophoretic mobilities of the constituents (metal and ligand), etc. However, such assumptions are no longer valid for high ionic strength since the apparent charge of the complex is lower than expected probably due to stabilization by ion pairing. As examples, the order of mobility for trivalent lanthanides in carbonate medium or the molecular actinides in oxalate solution does not follow the expected trend. Thus, assuming a charge of –3 for the heavy lanthanides (Ln(CO3)33–) and a charge of –5 for the lighter ones (Ln(CO3)45–); the lighter lanthanides exhibit a lower velocity despite a higher charge of their complexes. The magnitude of this effect depends on the nature of the counter-ion: chaotropic cations Cs+ and K+ lead to smaller shielding effect whereas for the kosmotropic cations Li+ and Na+ lower velocities are observed. Through all these examples, we highlight the necessity to solve several questions as: the effect of the ionic strength above 0.1 M, the shielding effect of the counter- ion, the relation describing the mobility change as a function of the number of ligand, the non-spherical shape of some complexes.

Calorimetric determination of enthalpy changes for the proton ionization of 3-[N-morpholino]propanesulfonic acid (MOPS), 4-[N-morpholino] butanesulfonic acid (MOBS) and 3-[N-morpholino]-2-hydroxypropanesulfonic acid (MOPSO) in water-methanol mixtures

JUMEAN, Fawwaz (American University of Sharjah) ;ABDO, Naser (American University of Sharjah) ; KHAMIS, Mustafa (American University of Sharjah)

Proton ionization enthalpies for three structurally related biological buffers, each with two ionizable protons, were determined using solution calorimetry. These buffers are 3-[N-morpholino]propanesulfonic acid (MOPS), 4-[N-morpholino]butanesulfonic acid (MOBS) and 3-[N-morpholino]-2-hydroxypropanesulfonic acid (MOPSO). Enthalpies were obtained in water-methanol mixtures with methanol mole fraction (Xm) from 0 to 0.360. The first ionization enthalpy (ΔH1) of all buffers was small (± 1.2 kJ mol-1) at all solvent compositions. The second ionization enthalpy (ΔH2) increased steadily with Xm, rising from 20.7 to 25.6 kJ mol-1 for MOPS, 26.3 to 31.0 kJ mol-1 for MOBS and 23.5 to 32.2 kJ mol-1 for MOPSO. The results are compared to those for related biological buffers. The observed variations are interpreted in terms of solvent- solvent and solvent-solute interactions.

[1] B.N. Bulos, F.H. Jumean, Thermochim Acta 411 (2004) 91. [2] F.H. Jumean, N.M. Abdo, Thermochim. Acta 447 (2006) 112. [3] F.H. Jumean, N.M. Abdo, Thermochim. Acta 448 (2006) 44. [4] F.H. Jumean, N.M. Abdo, M. I. Khamis, Thermochim. Acta 475 (2008) 22.

Synthesis and Preparation of Diethanolamine Functionalized Monodisperse Nanoporous Poly(HPMACl- EDMA) for Hydrophilic Interaction Chromatography

DİNÇ, Salİha (SELCUK UNIVERSITY) ; SAMATYA, Saba (Hacettepe University, Faculty of Engineering, Chemical Engineering Dept., 06532, Ankara/Turkey) ; TUNCEL, Alİ (Hacettepe University, Faculty of Engineering, Chemical Engineering Dept., 06532, Ankara/Turkey)

Monodisperse nanoporous hydrogel bead containing both reactive terminal chlorine and hydroxyl moieties have been prepared by a new multistage polymerization procedure so called “modified seeded polymerization”. The chemical modification of diethanolamine to this beads have been performed through terminal chroline moiety. The particles were used as a novel diol hydrophilic interaction stationary phase. The performance of the column was studied by the seperation of polar analytes which were chosen among purine and pyrimidine bases and nucleosides. The retention of the analytes was studied by varying asetonitril and ammonium acetate concentration, pH. The diethanolamine functionalized monodisperse poly(HPMACl- EDMA) column showed good selectivity for the seperation of the compounds concerned.

Enthalpies of Solution of 1,3,6,8-Tetrazatricyclo [4.4.1.13,8]dodecane as function of concentration and temperature

SALAMANCA BLANCO, Yina Patricia (Ph.D student) BLANCO CASTAñEDA, Luis H (Ph.D) ; VARGAS ESCAMILLA, Edgar F. (Sc)

The molar enthalpies of solution of 1,3,6,8-Tetraazatricyclo[4.4.1.13,8]dodecane, TATD, in water have been measured over the range of concentrations (0.005 to 0.04 mol kg-1) and as a function of temperature (278.15, 288.15, 298.15 and 308.15) K using an isoperibolic solution-reaction calorimeter[1]. The uncertainty of the experimental data was around 1%. The dependence of enthalpies on concentration and temperature are shown. The standard molar enthalpies of solution at infinite dilution have been calculated, their dependence on temperature is analyzed. The results are interpreted in terms of solute-solvent interaction. This work is part of the calorimetric study of molecules with potential pharmacological properties in aqueous solutions[2,3].

Keywords: Molar enthalpies of solution, TATD, Dilute solutions, Aqueous solutions.

References
[1] E. Vargas, J. Moreno, J. Forero, D. Parra, J. Therm. Anal. Calorim, 91 (2008) 659-662. [2] D.R. Torres, L.H. Blanco, F. Martínez, E.F. Vargas, J. Chem. Eng. Data, 52 (2007) 1700-1703. [3] L. Blanco, Y. Salamanca, E. Vargas, J. Therm. Anal. Calorim, 104 (2011) 209-212.

ATR-IR study on the concentration dependence of hydration number of alkali metal ions

KAMEDA, Yasuo (Yamagata University) ; AMO, Yuko (Yamagata University) ; USUKI, Takeshi (Yamagata University)

Infrared absorption spectra of uncoupled O-D stretching vibrational band of HDO molecule were measured for aqueous solutions involving alkali metal ions (Li+, Na+, K+ and Cs+) in order to investigate the concentration dependence of the hydration number of these ions. The double-difference IR method [1] was applied for observed ATR (attenuated total reflection)spectra to deduce the hydration number of constituent ions in the solutions.

It has been revealed that the number of water molecules in the first hydration shell of Li+, Na+, K+, and Cs+ for various counter ions are 6, 5, 6, and 8, respectively, in relatively dilute solutions of the concentration below 5 mol% MX (M: alkali metal ion, X: counter anion). Significant decrease in the hydration number was found for respective ions in more concentrated solutions above 10 mol% MX.

[1] O. Kristiansson, J. Lindgren, J. de Villepin, J. Phys. Chem. 92, 2680 (1988).

Physico-Chemical and Structural Characterization of the Binary System Phosphoric Acid – N,N-dimethylformamide

FADEEVA, Yuliya (Institute of Solution Chemistry of Russian Academy of Sciences); SAFONOVA, Lyubov (Institute of Solution Chemistry of Russian Academy of Sciences) ; PERSSON, Ingmar (Department of Chemistry, Swedish University of Agricultural Sciences)

The binary phosphoric acid (H3PO4) – N,N-dimethylformamide (DMF) system has very different physico-chemical properties depending on composition. The aim of the present study was to propose a detailed molecular model of the H3PO4-DMF system as a function of composition by combining previously reported physico-chemical data, conductometry (information whether ionic species are formed), viscometry (intermolecular interactions), and new structural studies as NMR (local environment) and infrared spectroscopy (strength of hydrogen bonding), and large angle X-ray scattering, LAXS (structure of chemical entities). The results from the theoretical simulation on the H3PO4-DMF system were used as a starting point for a detailed structure model. The proposed models for different H3PO4-DMF compositions was tested and extended by the results from the experimental physico-chemical observations.

Using the data of LAXS experiment the intermolecular distances in the mixture at two phosphoric acid concentrations (0.329 and 0.653 m.f.) were determined. The new proposed model can be described in the following way depending on H3PO4 molar fraction: 0.1 – 0.33 m.f. – monomeric and dimeric phosphoric acid, solvated by DMF, are both present, with increasing degree of dimers with growth of H3PO4 content; 0.33 m.f. – phosphoric acid is present as cyclic dimers solvated by four DMF molecules through strong hydrogen bonds but without any “inter-unit” interactions except van der Waal forces causing an effective packing, high density, low molar volume and low viscosity; 0.33 – 0.67 m.f. – phosphoric acid present as cyclic dimers, and the number of solvating DMF molecules shared by at least two phosphoric acid dimers decreases with increasing H3PO4 content reaching a mean number of four at 0.50 m.f. H3PO4, giving a polymeric layers structure, and a mean number of two at 0.67 m.f. H3PO4 giving a three-dimensional polymeric structure; 0.67 m.f. – three-dimensional structure of hydrogen bonded (H3PO4)2:DMF complexes forms providing the highest viscosity values; 0.67 – 0.80 m.f. – phosphoric acid present as cyclic dimers, and the number of solvating DMF molecules shared by at least two phosphoric acid dimers decreases with increasing H3PO4 content reaching a mean number of one at 0.80 m.f. H3PO4, giving a polymeric layers structure; 0.80 – 1.00 m.f. – excess of phosphoric acid causes that all OH groups in the phosphoric acid dimers can not hydrogen bind to DMF oxygen, and that the degree of OH groups hydrogen binding DMF decreases with increasing of H3PO4 content. Thus, it was established that the internal hydrogen bonding between pairs of phosphoric acid molecules in cyclic dimeric units is very important as well as the role of the DMF oxygen as hydrogen bond acceptor linking the dimeric phosphoric acid units into polymeric layers and three-dimensional networks.

This work was financially supported by Russian Foundation for Basic Researches (grant No 11-03-00311-a). The solution chemistry research by Ingmar Persson was supported by the Swedish Research Council.

Terahertz spectroscopy study of concentrated sorbitol solutions and glasses

SIBIK, Juraj (University of Cambridge) ; SHALAEV, Evgenyi (Pfizer Inc) ; SLATER, Nigel (University of Cambridge) ; ZEITLER, Axel (University of Cambridge)

The absorption and refractive index spectra of sorbitol water solutions were investigated in the temperature range of 80 to 293 K using terahertz time-domain spectroscopy (THz-TDS). Spectra were measured at frequencies 0.5-2.0 THz for two samples of sorbitol and water (70 wt% sorbitol and 30 wt% water, 50 wt% sorbitol and 50 wt% water) as well as pure water and pure amorphous sorbitol. For the samples of sorbitol/water solutions and pure sorbitol we observed a positive gradient when plotting the absorption coefficient at a single frequency with temperature. The gradient is increasing close to the expected calorimetric glass transition temperature Tg. Even stronger increase of absorption coefficient is observed after Tg. The increase in the absorption coefficient is related to an increase in the length-scale of regions involved in cooperative motion, e.g., increase in size of molecular clusters (sorbitol and/or water clusters). In contrast, the absorption coefficient of ice with temperature remained almost constant up to its melting point. The results show the sensitivity of terahertz spectroscopy to the changes in the size of molecular clusters that exhibit cooperative rotational and translational mobility. The results highlight the potential of this technique for the study of both aqueous solutions and glasses in particular with regards to better understanding in the effect of temperature on the structure and dynamics of aqueous solutions of sugars, which are commonly used for cryo- and lyo-protection of pharmaceutical products and of relevance in biological systems.

Interaction between charged surfaces mediated by molecules with spatially distributed charges

BOHINC, Klemen (Faculty of Health Sciences, University of Ljubljana)

The interaction between highly charged systems could not be described by the mean field theory. More advanced methods have to be used in order to introduce the correlations between highly charged particles. In this work I focus on the system of highly charged surfaces (1), separated by a solution of molecules with spatially distributed charge (2). Two different representations of the molecular shape will be considered: rod-like and spherical. The system will be theoretically described by the functional density theory. For sufficiently long molecules and large surface charge densities an attractive force between like surfaces arises due to the spatially distributed charges within the molecules (2, 3). The added salt has influence on the condition for the attractive force between like charged surfaces (4). The theoretical results will be compared with Monte Carlo simulations (2, 5). Recent measurements with multivalent rigid rod like particles will be discussed.

References:

(1) S. Maset, K. Bohinc, J. Phys. A 2007, 40, 11815. (2) S. May, A. Iglič, J. Reščič, S. Maset, K. Bohinc, J. Phys. Chem. B 2008, 112, 1685. (3) M.M. Hatlo, K. Bohinc, L. Lue, J. Chem. Phys. 2010, 132, 114102. (4) K. Bohinc, J. Reščič, S. Maset, S. May, J. Chem. Phys. 2011, 134, 074111-1. (5) J.M. Grime, M.O. Khan, K. Bohinc, Langmuir, 2010, 26(9) 6343.

X-ray and neutron scattering study of aqueous solutions of polyhydroxycompounds

SHALAEV, Evgenyi (Pfizer Inc) ;CHOU, Shin Grace (National Institute of Standards and Technology, Gaithersburg, MD 20899, USA) ; SOPER, Alan (STFC Rutherford Appleton Laboratory, ISIS Facility, Didcot, UK) ; KHODADADI, Sheila (National Institute of Standards and Technology, Gaithersburg, MD 20899, USA) ; CURTIS, Joseph E. (National Institute of Standards and Technology, Gaithersburg, MD 20899, USA) ; KRUEGER, Susan (National Institute of Standards and Technology, Gaithersburg, MD 20899, USA) ; NARAYANAN, T (European Synchrotron Radiation Facility, Grenoble, France)

Polyhydroxycompounds (i.e., sugars and sugar alcohols) are widely used to improve stability of pharmaceutical and biotechnological products during manufacturing and storage. In this study, we apply synchrotron-based small and wide angle X-ray scattering (SAXS and WAXS), as well as small- and wide-angle neutron scattering (SANS and WANS) measurements, to study the structure of concentrated aqueous solutions of sorbitol and sucrose at different temperatures. For sorbitol-water system, the analysis of the neutron data suggests that water forms tetrahedral-like clusters of molecules within the sorbitol matrix. Note that the local structure of sorbitol matrix (represented by RDF obtained from WANS) was similar in the entire temperature range studied, from 100K to 300K, whereas some changes in the structure of water clusters were observed at lower temperatures. Local structure of water clusters in water-sorbitol system resembled the structure of low-density amorphous ice. Large- scale inhomogeneities were detected by both SAXS and WANS measurements at lower temperatures in both sorbitol and sucrose systems. These inhomogeneities represent areas with sharp interfaces, potentially indicative of molecular segregation between water and sugar on the length scale of tens nms, although neither water nor sugar crystallization was observed. Overall, the appearance of large (i.e., tens of nms) segregated structures at lower temperatures is likely due to coalescence of smaller "clusters" of water and /or sugar, without any major structural changes on the smaller lengthscale of several nm.

Unravelling hydration properties of lanthanoids and actinoids cations in water: an interplay between experiments and theory

SPEZIA, Riccardo (CNRS, LAMBE UMR 8587 CNRS, CEA, Université d'Evry Val d'Essonne)

In order to have a microscopic understanding of phenomena related to solution chemistry, a fundamental (yet challenging) problem is the accurate modeling of ion hydration structure and dynamics. At this aim, theoretical and computational progress is still needed. The accurate interaction description must be coupled with a correct statistical sampling to address liquid properties. Approximate models are thus necessary. The simple molecular models with fixed charges are thus slowly being replaced by models which take into account higher order terms in the electrostatic expansion. Particularly challenging systems are those containing charged (or highly charged) particles where water polarizability must be taken into account. Actinoids and lanthanoids highly charged bare cations, 3+ or 4+, are studied in water by developing polarizable classical interaction potentials. Our models are able to explain hydration properties of most of them at different conditions of temperature and concentrations [1-3]. In particular structural and dynamical properties are investigated and a connection between experiments and microscopic properties is done. Via an accurate and systematic comparison between polarizable molecular dynamics simulations and XAS (both EXAFS and XANES) experiments, we are able to provide for hydration of the whole lanthanoid series: (i) an interaction model in perfect agreement with experimental observations, (ii) a novel set of effective ionic radii that can replace the Shannon's radii obtained in solid state currently used [4], and (iii) insights on the second hydration shell. Also the trend of lanthanoids(III) diffusion coefficients in water is explained in terms of our results (being in agreement with experiments) and explained. Some of the theoretical foundations are also discussed, in particular the link between simulation parameters and atomic properties.

1) M.Duvail, P.Vitorge and R.Spezia. J. Chem. Phys. 130, 104501, (2009). 2) M.Duvail, P.Vitorge and R.Spezia. Chem. Phys. Lett. 498, 90-96 (2010). 3) C.Beuchat, D.Hagberg, R.Spezia and L.Gagliardi. J. Phys. Chem. B 114, 15590–15597 (2010). 4) P.D'Angelo, A.Zitolo, V.Migliorati, G.Chillemi, M.Duvail, P.Vitorge, S.Abadie and R.Spezia. Inorg. Chem. 50, 4572–4579 (2011).

Study of the EDTA speciation for its quantification in radioactive wastes containing heavy metals

RENAUDIN, Laëtitia (LANIE du CEA de Saclay) ; DU BOIS DE MAQUILLé, Laurence (LANIE du CEA de Saclay) ; GOUTELARD, Florence (LANIE du CEA de Saclay) ; VIAL, Jérôme (LSABM de l'ESPCI) ; JARDY, Alain (LSABM de l'ESPCI) ; THIéBAUT, Didier (LSABM de l'ESPCI)

EDTA (Y), a chelating agent that was used for decontamination processes, affects radioelement mobilities in environment. Its quantification is required for nuclear waste management.

Ion-pair chromatography with mass spectrometry detection is a convenient method for Y analysis. The counter ion is tributylammonium and Y should be present under a single anionic chelate form. However, radioactive wastes contain many heavy metals and Y is present as several chelates. Speciation studies as a function of pH were carried out by computer simulation in order to choose a metal cation to be added in excess to the solution to get a major chelate form, for lack of only one. Fe3+ and Ni2+ were tested. As ferric hydroxide precipitated in the chromatographic analysis conditions, Ni2+ was chosen. Nevertheless, as attested by simulation distributions, its use implied a basic pretreatment of the solution to be analyzed in order to eliminate iron and some other heavy metals as hydroxides before pH adjustment and nickel addition after centrifugation.

A good agreement was observed with experimental results using deuterated EDTA. This new approach based on a speciation study allowed, for the first time, analyzing EDTA in real samples resulting from nuclear liquid waste processing.

Sorption of gold(III) on mercapto modified rice hull ash silica

NURYONO, Nuryono (Dept of Chemistry, Gadjah Mada University, Yogyakarta, Indonesia) ; RUSDIARSO, Bambang (Dept of Chemistry, Gadjah Mada University, Yogyakarta, Indonesia) ; C.W. SAKTI, Satya (Dept of Chemistry, Gadjah Mada University, Yogyakarta, Indonesia) ; HAMDINI, Saprini (Department of Chemistry, Faculty of Mathematics and Natuiral Sciences, Mataram University, Mataram, Indonesia)

The content of gold in mineral is very low and the distribution is not homogeneous. Therefore for determination of gold with high sensitivity is necessary to develop a method of pre-concentration and separation before detection. Recently silica (MMS) was synthesized using sol-gel process with precursor of sodium silicate solution , various sorbents including modified silica for those purposes have been widely used. In this research, adsorption-desorption of Au(III) on rice hull ash (RHA) silica modified with mercaptopropyltrimethoxysilane in a batch system has been studied. The adsorbent of mercapto modified prepared from destruction of RHA. Adsorption was carried out by mixing a solution of metal ions and adsorbent with variation of pH, contact time, and concentration of ions. Parameters of kinetics (rate constant and order) and thermodynamics (capacity and adsorption constant) were evaluated with appropriate models. Desorption was emphasized by mixing of adsorbent containing metal ions and desorbing solution of thiourea solution in HCl with variables of contact time, and desorbing solution concentration. Adsorption on MMS was not changed in a pH range of 2 – 6. Kinetic study demonstrated that for Au(III) ion both adsorption and desorption with 1 M thiourea solution in 1 M HCl follows pseudo-second order with the adsorption rate constant of 10.0x10-3 g/mg.min and the desorption one of 14.0x10-3 g/mg.min. Adsorbent produced is selective for Au(III) from Cu(II) and Ni(II) and the capacity (in a range of 203 – 212.8 mg/g) is not affected with the presence of other metals. The Au(III) adsorbed in MMS is completely desorbed with 1 M thiourea solution in 1 M HCl within 24 hours and the capability of the solution to leach Au(III) is decreased with presence of Cu(II) and Ni(II). The results demonstrated that adsorption capacity of Au(III) on MMS is quite high and adsorption–desorption could occur very fast. Therefore, there is good prospect for MMS in applications for the solid phase extraction of Au(III) from Cu(II) and Ni(II) in analysis purposes.

The role of water in conformational transitions of peptides

NERUKH, Dmitry (Aston University)

MD simulated dynamics of L-alanyl-L-alanine zwitterion in explicit water has been analysed with the main emphasis on the moments of conformational transitions of the peptide. The system exhibits three well separated stable conformational states that were defined as areas on the plot of two dihedral angles of the peptide's backbone.

We study one of the transitions that happened 353 times during the 1 microsecond simulation. The transitions themselves take only ~5 picoseconds time, therefore, the popular Markov State Model could not be used. Instead, we used a hidden Markov model to analyse the sequences of the metastable states that are inherently non- Markov. This allowed us to obtain a statistically correct picture with the time resolution of 0.3 picoseconds. Since no transitions take place in vacuum, the surrounding water is the key factor that makes the transitions possible. We have analysed the density of water at the stable conformations and during the transitions at various moments up to 100 picoseconds in advance of the transition. We have found that

- ~5 picoseconds before the transition, that is when the dihedral angles change their values the most, the water density significantly reduces (up to two times);
- the change of water density begins at ~50 picoseconds before the transition, 10 times earlier than changes in the angles occur!
- during the transition the dynamics of water density becomes highly correlated with the dynamics of the angles, which is completely absent during the stable conformations periods.

We conclude that the transitions are characterised by highly correlated dynamics of water involving at least two solvation shells and initiated an order of magnitude earlier than the changes in the peptide molecule itself.

A new insight into structures of concentrated associated salt aqueous solutions: combination of thin-film Ultra-violet spectroscopy and TD-DFT calculation

ZENG, Dewen (College of Chemistry and Chemical Engineering, Central South University, 410083 Changsha, P.R.China) ; ZHANG, Ning (College of Chemistry and Chemical Engineering, Central South University, 410083 Changsha, P.R.China) ; VOIGT, Wolfgang (Institute für Anorganische Chemie, TU Bergakademie Freiberg, 09596 Freiberg, Germany)

Structure information for concentrated heavy metal chloride solutions determined by different methods, such as neutron diffraction [1], EXAFS [2-4] and Monte Carlo [5-7], are usually inconsistent with each other. In this case, a new method has been proposed to recognize the solution structures, which is the combination of thin-layer ultraviolet spectroscopy and time-dependent density function theory [8-10]. The former enable the ultraviolet measurement on concentrated solution and consequently the electron spectra of assigned species and the latter can give electron spectra of species with fine structures. An example was given on the structure analysis on pure CuCl2 aqueous solution and the mixture of CuCl2+NaCl+H2O. The results obtained in this new method were compared with those determined by other structure methods.

References [1] Ansell, S.; Tromp, R. H. et al. J. Phys.: Condensed Matter 7, (1995) 1513-1524. [2] Bell, J. R.; Tyvoll, J. L. et al. J. Amer. Chem. Soc. 95, (1973) 1456-1459. [3] D'Angelo, P.; Botteri, E. et al. J. Chem. Phys 107(8), (1997) 2807-2812. [4] Collings, M. D.; Sherman, D. M. et al. Chem. Geol. 167, (2000) 65-73. [5] Rode, B. M.; Islam, S. M. J. Chem. Soc. Faraday Transactions 88, (1992) 417-422. [6] Texler, N. R.; Rode, B. M. Chem. Phys. 222, (1997) 281-288. [7] Texler, N. R.; Holdway, S. et al. J. Chem. Soc., Faraday Trans. 94, (1998) 59-65. [8] Xia, F. F.; Yi, H. B.; Zeng, D. J. Phys. Chem. A 113, (2009) 14029–14038. [9] Xia, F. F.; Yi, H. B.; Zeng, D. J. Phys. Chem. A 114, (2010) 8406–8416. [10] Xia, F. F.; Yi, H. B.; Zhou, Q.B.; Zeng, D. J. Phys. Chem. A 115, (2011), 4416-4426.

Effect of CaCl2 on the Self Aggregation of Serotonin Norepinephrine Reuptake Inhibitor drug Venlafaxine HCl over Temperature Range 298.15-313.15 K

JAMAL, Muhammad Asghar (Government College University Faisalabad) ; SHAHZAD, Khurram (Government College University Faisalabad) ; MASOOD, Feroza (Government College University Faisalabad)

The aggregation characteristics as well as the voluetric behavior of Venlafaxine HCl have been determined. The effect of the added salt on the aggregation characteristic have been studied whether the crticle micelle concentration of the drug is affected by the addition of the salt which have implication in the transport rate of the drug in the living organisms.
The aggregation characteristics of Venlafaxine HCl, an amphiphilic serotonin norepinephrine reuptake inhibitor antidepressant drug, have been investigated in water and 0.01 mol/Kg CaCl2.2H2O solutions. Apparent molar volumes and apparent molar compressibilities have been computed by using density and sound velocity data obtained from Anton Paar density sound analyzer (DSA 5000). The critical micelle concentrations of this drug were obtained from ultrasound velocity measurement by using recently developed least square fitting algorithm. Negative deviations from Debye-Huckel limiting law of apparent molar volume for this drug was obtained over the temperature range studied showing no pre-association below the critical micellar concentration. The compressibility data has been used to discuss solvent-aggregate interactions. Partial molar expansivity, E0, and second derivative values, (∂2V0/∂T2), have also been estimated.

Molecular models of natural organic matter and its colloidal aggregation in aqueous solutions: Challenges and opportunities for computer simulations

KALINICHEV, Andrey (Ecole des Mines de Nantes)

Natural organic matter (NOM) is ubiquitous in the environment and plays many important geochemical roles by forming aqueous complexes of widely differing chemical and biological stabilities with various inorganic and organic species. Metal-NOM interactions induce strong correlations between NOM concentration and the speciation, solubility and toxicity of many metals in the environment. In the processes of water purification and desalination, NOM is also implicated in being the major foulant of nanofiltration and reverse osmosis membranes, either directly or by forming a surface conditioning layer for microbial attachment ("biofouling"). Despite significant geochemical, environmental and industrial interest, the molecular-scale mechanisms and dynamics of the physical and chemical processes involving NOM are not yet well understood. Computational molecular modeling can be an ideal tool to study these phenomena in true atomistic detail at nano-scale in both space and time. Yet, this route presents significant challenges due to the extraordinary compositional and structural diversity of NOM which preclude a unique definition of its molecular structure.

This talk will provide a brief overview of the challenges and opportunities for the application of computational molecular modeling to NOM-related problems with specific focus on developing quantitative tools for structural, dynamic, end energetic characterization of metal-NOM complexation, hydration, hydrogen bonding, hydrophobic interactions, and colloidal aggregation in aqueous solutions based on the molecular dynamics (MD) computer simulations using relatively simple, but reasonably realistic model fragments of NOM. The modeling predictions from large-scale MD simulations of the effects of various metal cations on NOM aggregation in aqueous solutions will be compared with experimental data on dynamic light scattering (DLS) and small angle neutron scattering (SANS) using Suwannee River NOM (SRNOM) samples. The DLS data for Ca2+–NOM suggest the formation of a wide range of colloidal aggregates with sizes between 100 and 1,000 nm. In contrast, Mg2+ and Na+ do not seem to affect the aggregation of SRNOM as strongly. SANS data appear inconclusive, but also indicate the presence of quite large (>50 nm) fractal particles formed presumably through a cluster-cluster aggregation. The MD simulation results qualitatively agree with these observations, but also point out to the need for simulations at much larger time and length scales with more complex NOM models in order to fully capture the diversity of molecular processes involving NOM.

On the use of high precision conductimetry of ionic mixtures to determine the effective charge and size of nanocolloids. Application to the complexation by humic substances of small cations.

MéRIGUET, Guillaume (UPMC) ;DURAND-VIDAL, Serge (UPMC) ; ROGER, Gaelle (ONERA) ; ROGER, Gaelle (ONERA) ; BERNARD, Olivier (UPMC) ; ANCIAN, Bernard (UPMC) ; TURQ, Pierre (UPMC)

France is currently directing a research program aiming at providing the necessary data for assessing the feasibility of a deep reversible geological storage for High- Level and Long Lived nuclear waste at a depth of 500 m in the East of the Paris basin. In order to ascertain the safety of such a disposal, a comprehensive study of ionic mobility in the clay host rock formation (Callovo-Oxfordian) is carried out [1]. It has been proved that the exposition of the host rock to concrete generates fulvic and humic acids [2]. The formation of these compounds is due to the degradation of the Natural Organic Matter (NOM) in the alkaline medium of the Excavation Damaged Zone.

The mobilization of radionuclide by NOM is complex and still badly understood. It is affected by several factors such as chemical and physical properties of NOM, ionic strength and pH of the environment, nature of the pollutants, etc. Two parameters are fundamental to understand the behavior and the physico-chemical properties of degraded NOM particles: the radius R and the charge Z. These parameters were determined using high precision conductivity experiments and an appropriate theoretical approach.

Indeed, the size of the humic substances strongly influences its mobility and its negative charge facilitates the complexation of positive pollutants that could be desorbed from the clays. In order to optimize an experimental protocol, we analyzed reference humic acids and polyacrylic acid, which is considered as a good analogue of humic acids.

These reference humic substances have also been studied in the presence (or absence [3]) of several ionic species: NaCl, CaCl2, MgSO4, etc. that are naturally present in the poral water of the Callovo-Oxfordian [4]. Sizes and effective charges of reference humic substances measured in these various conditions of ionic strength will be discussed together with AFM, DLS, NMR and laser zetametry measurements. [1] B. Rotenberg et al Modelling water and ion diffusion in clays: A multiscale approach. C. R. Chimie 10 (2007) 1108. [2] F. Claret et al Generation of humic and fulvic acid from callovo-oxfordian clay under high alkaline conditions. Sci. Tot. Env. 317 (2003) 189. [3] G. M. Roger et al Characterization of humic substances and polyacrylic acid: A high précision conductimetry, Colloid and Surface A, 358 (2010) 51-57. [4] A. Vinsot et al In situ characterization of the callovo-oxfordian pore water composition. Phys. Chem. Earth 33 (2008) 75.

A Computational Approach to Solvent Properties; Measures of Lewis acidity and Basicity

WAGHORNE, Earle (University College Dublin) O'FARRELL, Christina (University College Dublin)

It has long been recognized that the short range interactions between solute and solvent molecules are central to solvation. This is well illustrated by the success of numerous multi-parameter relationships, having the general form: $Y = Y0 + aA + bB + cC \cdots$
Where Y represents a solvation related parameter, A, B and C represent solvent properties and the corresponding coefficients a,b, and c indicate the importance of the corresponding solvent parameters to Y for the particular solute. Among the most direct solvent parameters are those that measure Lewis acidity or basicity. These include, for example, Gutmann's donor and acceptor numbers, Swain et al.'s acity and basity and Kamlet and Taft's hydrogen bond acidity and basicity, among others. Computational methods, in principle, provide several routes to predicting these solvent parameters and to accounting for differences in these scales. Thus, for homologues, the Gutmann donor number shows excellent linearity with calculated energies of the filled frontier orbitals but these correlations do not overlap, reflecting both size and steric effects. In this paper we present the results of extensive calculations directed at providing a more quantitative description of the factors that determine these experimental solvent parameters and explore the extent to which they can be predicted from such calculations.

Leaching of sulfide ores with solutions containing natural organic acids

NOVIKOVA, Svetlana (Novosibirsk State University, Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences)

Oxidation of sulfide minerals in mine tailings creates a potential threat of the ground- and surface water contamination by toxic heavy metals. Humic and fulvic acids being present in natural waters can form soluble or insoluble metal-complexes and enhance or reduce the metal mobility. Currently the problem of humic substances (HS) effect on metal migration and precipitation is actually relevant. The aim of the present study is to determine the influence of naturally occurring chelating agent, namely fulvic acid (FA), on the release of Fe and Cu from pyrite- chalcopyrite ores (Tuva Region, Russia). The experimental sulfide dissolution was carried out using water (solution 1), aqueous (380 mg/L FA, solution 2) and alkaline (1800 mg/L FA, solution 3) extracts of peat. The interaction of solutions with ore samples were attained by performing batch sorption experiments, where all solutions were added to ore samples maintaining the solid-solution ratio of 1:100. The experiment was doing during 2 months in conditions simulating semiarid climate then the solutions were subjected to metal analyses by AAS, ICP-AES and pH control. Despite of initial H+-ion release during the sulfide oxidative leaching, the pH followed by a further increase due to the calcite film dissolution. In the solution 1, Fe and Cu precipitated as hydroxides, whereas in the presence of FA they were accumulated in the solution (Fe ~ 3.8 and ~ 6.6 mg/L, Cu ~4,3 and ~7,2 mg/L in solutions 2 and 3, correspondingly) through the formation of soluble metal-organic complexes. According to thermodynamic calculations by WATEQ4F1, the amounts of the components in the organic complex form in total metal content in solution were 59% Fe and 99% Cu (solution 2) in the final analysis. This is due to the strong iron ability to hydrolysis, even considering the stability constant of iron-fulvic complex is an order of 3 larger than those of copper-fulvic complex. It was found that the release of metals in solution is mainly dependent on fulvic acid concentration and solution pH. At a solid-solution ratio of 1:100 it was the formation of leach solutions containing Cu and Fe above the maximum allowable concentration for drinking water, which reveals one of the causes of environmental pollution by sewage comprising toxic metals. Even in the presence of calcite as neutralizer of acidic solutions during sulfide ores oxidation, the pH increase didn't promote the heavy metal precipitation and leaching solution wash-out if they involve a high concentration of natural organic acids.

1. Ball, J.W., Nordstrom, D.K., 1991. User's Manual for Wateq4F, with Revised Thermodynamic Database and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters. US Geol. Surv., Menlo Park, Cal.

The Use of Models to Understand the Chemistry of Actinoids

VITORGE, Pierre (Laboratoire Analyse et Modelisation pour la Biologie et l'Environnement, UMR 8587, Univ Evry, CNRS, CEA, and: CEA, DEN, DPC, SECR, LSRM) ; QUéMET, Alexandre (CEA/DEN/DPC) ; MARSDEN, Colin (Université Paul Sabatier, Toulouse) ; SIBOULET, Bertrand (CEA/DEN, ICSM) ; DUVAIL, Magali (Andra, UPMC, PECSA UMR 7195)

The chemistry of actinoids and several radionuclides are studied to predict their migrations in deep groundwaters. The scientific bases for predicting such chemistry in equilibrium conditions at trace concentrations are well established and accepted, while models are still debatable for more concentrated solutions (activity coefficients), or for the retention of pollutants in (co-precipitation) or on (sorption) solids. It is here shown how thermodynamic concepts developed for solution chemistry can very well be extended to co-precipitation (solid solutions or equivalently solid mixtures) and sorption on surfaces (ionic exchange, surface complexation). Furthermore, the numerical values of thermochemical data reflect chemical reactivity. Conversely, qualitative chemical concepts can help understanding the numerical values of typically complexing constants: namely, complexing constants often reflect the hard character of the f-block cations. Hardness certainly explains the success of simulations based on classical molecular dynamics. Nevertheless, actinoids in high oxidation states can as well form covalent ions, which needs quantum level of modeling. Quantum modeling indeed recently explained the exceptional chemical behavior of Pa, the actinoid element between Th and U. This qualitative use of quantum calculations is here illustrated together with their potential use for open chemical questions on f-block elements.

An Experimental Atomistic Study of the Cryoprotectant Glycerol in Aqueous Solutions

TOWEY, James (University of Leeds) ; DOUGAN, Lorna (University of Leeds) ; SOPER, Alan (ISIS Facility, Rutherford Appleton Laboratory)

The sugar alcohol, glycerol, has been of significant scientific interest for many years due, in part, to its ability to act as a cryoprotective agent (CPA). A long- standing hypothesis for the action of CPAs is that they act by modifying the water structure around biological molecules. A necessary first step toward determining the stabilizing mechanism of CPAs, such as glycerol, is to test this hypothesis by directly examining glycerol's impact on water structure. We have completed a series of neutron diffraction experiments combined with computational modelling to obtain atomistic level structural information on aqueous glycerol across the concentration range. Our studies of pure glycerol have shown that this molecule does not contain intra-molecular hydrogen bonds and has a larger number of inter-molecular hydrogen bonds than previously suggested. Examination of a concentrated glycerol solution has shown that water molecules preferentially bind to glycerol molecules rather than other water molecules leading to an abundance of isolated water molecules. Our studies of a dilute glycerol solution demonstrate that, while the local structure of water is relatively unperturbed by the presence of glycerol, the hydrogen bonded network is highly mixed. The efficient integration of glycerol into the dilute solution results in a diminished ability of water to form an extended hydrogen bonded network. Our results demonstrate that efforts to explain solute effects on protein stability should focus on not just local water structure but the extended hydrogen bonded network of the system.

Apparent Molal Volumes of 1,3,5,7-Tetraazatricyclo[3.3.1.1(3,7)]decane and 1,4,6,9-Tetrazatricyclo(4.4.1.1.4,9)dodecane in Aqueous Solution as a Function of Temperature

VARGAS, Edgar (Universidad de los Andes) ; SALAMANCA, Yina (Universidad Nacional de Colombia) ; BLANCO CASTAñEDA, Luis (Universidad Nacional de Colombia)

The densities of 1,3,5,7-Tetraazatricyclo[3.3.1.1(3,7)]decane, HMT, and 1,4,6,9-Tetrazatricyclo(4.4.1.1.4,9)dodecane, TATD, have been measured in water in concentration ranges between 0.005 to 0.04 mol•kg-1 at (278.15, 288.15, 298.15 and 308.15) K using a magnetic float densimeter. The experimental uncertainty was ± 0.000001 g•cm-3. The apparent molar volumes were calculated. The dependence of partial molar volumes at infinite dilution with temperature is shown and the molar expansibilities are also calculated. Van der Waals Volumes, cavity volumes and "interaction" volumes were calculated and the results have been discussed in terms of solute – solvent interactions.

Enthalpies of solution of Calix[4]resorcinarene in non-aqueous solvents as a function of concentration and temperature.

RIVEROS SANTOYA, Diana Carolina (Universidad de los Andes) ; VARGAS, Edgar (Universidad de los Andes) ; MARTINEZ, Fleming (Universidad Nacional de Colombia)

The enthalpies of solution of 2,8,14,20-tetrametil-4,6,10,12,16,18,22,24 octahidroxiresorci[4]areno, calix[4]resorcinarene 1, have been measured in methanol, ethanol and propanol at (288.15, 298.15 and 308.15) K using a isoperibol calorimeter. The enthalpies of solution at infinite dilution and their dependence with temperatures were calculated for each solvent. Enthalpies of transference of calix[4]resorcinarene between solvents were calculated and the results were interpreted in terms of solute – solvent interactions.

Extraction and quantification of organic phosphorus in compost, soil and sediment

PARASKOVA, Julia (Uppsala University) SJöBERG, Per (Uppsala University) ; RYDIN, Emil (Uppsala University)

Understanding the dynamic flux of phosphorus in the environment is important due to the key role it plays in eutrophication. A substantial part of the phosphorus lost from soils may be organically bound. The speciation of different organic phosphorus forms, however, has thus far

been difficult as traditional fractionation schemes measure phosphorus with respect only to its chemical bonding. In this project, established methods for the extraction of nucleic acids and phospholipids have been combined with molybdate colorimetry to provide a simple and relatively inexpensive scheme for the quantification of specific fractions of organically bound phosphorus. The method has been tested on composted animal manure, lake sediment and both fertilized and unfertilized agricultural soil. Initial findings show that nucleic acid bound phosphorus comprises up to 1% by weight of the total phosphorus content in compost, up to 3% in sediment, and around 2% in fertilized soil. The values for phospholipid-P are 0.1%, 0.5%, and 0.2% for compost, sediment and soil, respectively. The next step is to determine whether these organic phosphorus fractions will be mineralized in the aquatic environment and whether the mobilized phosphorus supports aquatic eutrophication.

Properties of Hydrated Alkali Metal Ions in Aqueous Solution

MäHLER, Johan (SLU) ; PERSSON, Ingmar (SLU)

The structures of the hydrated alkali metal ions in aqueous solution have been studied by large angle X-ray scattering, and the hydrogen bonding with infrared spectroscopy. The observed M-O distances have been compared with available crystal structure data of hydrates and complexes with other relevant non-constraining neutral oxygen donor ligands. By subtracting the known radius of water oxygen1 from the average of relevant crystal structure M-O distances, improved ionic radii have been obtained. These differ in some cases by 0.05 Å from those proposed by Shannon.2 Shannon used oxide and fluoride structures where the small alkali metal ions occupy holes in the close-packed structures where the coordination of the metal ions is controlled by the close-packing rather than the preferred coordination chemistry of the metal ion. This resulted in ionic radii of the small alkali metal ions differing a lot, on the other hand, the larger ones, which cannot be close-packed due to similar size as the oxide and fluoride ions, are in good agreement with our newly developed ionic radii. The water molecules hydrating the larger alkali metal ions are spectroscopically indistinguishable from bulk water molecules, while the water molecules hydrating the lithium and sodium ions are observed.

Insights into the interaction of some antibiotic drugs with serum albumin: Biophysical aspects

CHOUDHARY, Sinjan (Indian Institute of Technology Bombay) KISHORE, Nand (IIT Bombay)

The work describes a combination of calorimetric and spectroscopic approach to understand drug-protein interactions. The binding thermodynamics of some antibiotic drugs has been addressed alongwith the conformational changes occurring in the serum albumin as a result of binding. The binding thermodynamic parameters, and nature of interactions provide role of various functional groups on the drug and protein in the binding process and hence provide guidelines to synthetic chemists in synthesizing the target oriented drugs.

The binding interactions of tetracycline, rolitetracycline, and lincomycin have been investigated by using isothermal titration calorimetry, differential scanning calorimetry, steady state and time resolved fluorescence, circular dichroism, and uv- visible spectroscopies. The binding constants, enthalpies, entropies, free energies, and stoichiometry of binding have been obtained. The results on the binding of tetracycline and rolitetracycline with bovine serum albumin were best represented by a sequential binding site model. The values of the binding constant were of the order of 104 and 103 respectively, for tetracycline and rolitetracycline. Lincomycin did not show any binding pattern. However, the surfactants modified conformational state of the protein showed weak binding pattern. The binding parameters were also determined by steady state and time resolved fluorescence spectroscopy. The influence of ionic and mixed hydrophilic-hydrophobic character additives on the binding was studied to understand the type of interactions between drugs and the protein. Combinatorial studies on the binding of these drugs in presence of each other and warfarin allowed us to understand the possible and overlapping binding sites on the protein. The results have provided quantitative and qualitative understanding of the binding of these drugs with serum albumin and hence help in providing guidelines to synthesize target oriented drugs.

Quantitative and qualitative characterization of the partially folded states of proteins: Calorimetric and spectroscopic investigation

SHARMA, Nand Kishore (IIT Bombay)

We have demonstrated that isothermal titration calorimetry can be effectively used to characterize the partially folded states of the proteins. Traditional spectroscopic measurements can give qualitative information, however, with the advancement in the sensitivities of the microcalorimeters, it has been possible to get further fine details such as common structural features of the molten globule states of different proteins. We have used a biophysical approach to understand the protein folding intermediates.

Understanding the protein folding mechanism and interaction of proteins with solvents is extremely important as important tasks in the living cells are carried out by the proteins. Therefore the characterization of protein folding intermediates has attracted considerable interest. The enhanced fluorescent intensity upon binding of 8-anilino-1-naphthalene sulphonate (ANS) to the proteins has been routinely used as one of the criterion to characterize their partially folded states. We have demonstrated that isothermal titration calorimetry can be effectively used to characterize the partially folded states qualitatively and quantitatively from the titration of ANS with the native, partially folded and denatured states of the protein. The binding of ANS with the molten globule states and conformational characterization of a-lactalbumin, cytochrome c, myoglobin, bovine serum albumin, and and concanavalin A have been studied by using a combination of isothermal titration calorimetry, fluorescence, circular dichroism spectroscopies and dynamic light scattering measurements. The ITC results indicate that binding of ANS to molten globule states generated in proteins under different solvent conditions such as low pH, salts, and alcohols displays heterogeneity with two classes of non-interacting binding sites. The thermodynamic parameters of interaction have permitted discussion on general features of the molten globule states of these proteins.

Reaction Thermodynamics for Ionization of Acetic Acid in Protic Ionic Liquid, Ethylammonium Nitrate

KANZAKI, Ryo (Kagoshima University) ; SONG, Xuedan (Kyushu University) ; UMEBAYASHI, Yasuhiro (Kyushu University) ; ISHIGURO, Shin-ichi (Kyushu University)

Thermodynamic parameters, pKa (DG°), DH°, and DS° of acid-dissociation (ionization) of acetic acid has been determined by means of potentiometric and calorimetric titrations in neat ethylammonium nitrate (EAN), which is a typical protic ionic liquid (PIL). The pKa value is larger in EAN than in water because HNO3 acts as an acid (proton donor) in EAN instead of H3O+ in water. The ionization enthalpy and entropy in EAN are quite different from those in water. This indicates the solvation state of acetic acid undergoes an exceptional change through ionization in comparison to that in water.

Nitrate Coordination with Eu3+: influence of the solvent on the nature of the ion pair

GUILBAUD, Philippe (CEA) DUVAIL, Magali (UPMC)

Understanding the solvation properties of heavy metal ions, such as lanthanide (Ln3+) and actinide (An3+) cations, is the first step to address their physical and chemical properties in solution. In these solutions, their structural and thermo- dynamical properties depend directly on the nature of the solvent and on the presence of counter-ions and/or ligands in the vicinity of the cation. In the framework of the nuclear fuel recycling (where Ln3+ and An3+ cations are present), nitrate anions are fundamental since the fuel is dissolved in concentrated nitric acid solution before the liquid-liquid extraction separation processes. In this study, the coordination of nitrate anions with Ln3+ has been investigated in water, methanol and octanol-1 using molecular dynamics simulations with explicit polarization. Potential of mean force (PMF) profiles have been calculated for Ln(NO3)2+ in these solvents using umbrella- sampling molecular dynamics. In pure water, no huge difference is observed in the nitrato coordination of 3 lanthanide ions (Nd3+, Eu3+ and Dy3+), i.e. the nitrate anion is either dissociated, or bonded to the cation with a monodentate coordination. Then, the influence of the nature of the solvating molecules on the nitrato coordination has been investigated for Eu3+. PMF profiles point out that both monodenate and bidentate coordination modes may be stable in neat methanol, while in neat octanol, only the bidentate one is. MD simulations of Eu(NO3)3 have then been performed in water–octanol mixtures with different concentrations of water. These simulations confirm the importance of the water molecules' presence on the nitrate ion's coordination mode.

Excess Electrons in Water: What Can We Learn from Molecular Dynamics Simulations?

TURI, László (Institute of Chemsitry, Eötvös Loránd University)

In the present talk we will overview the results of a series of mixed quantum- classical molecular dynamics simulations, examine the physical properties of hydrated electron systems and compare our results to available experimental data. The discussion will focus on the the most basic aspects of the physics of these systems. In particular, we examine the traditional cavity model of the hydrated electron.

Excess electrons are known to stabilize in water as hydrated electrons. Hydrated electron systems with reduced dimensionality, such as negatively charged, finite size water clusters, and excess electrons at water/air interfaces, have also been studied for a while. The fundamental research interest of these systems lies in the challenge for the proper description of the interaction between the most important solvent, water and a truly quantum mechanical object, an electron. An excess electron in water may also be considered as a useful model for studying key energetic, structural and dynamic aspects of complex phenomena (i.e. solvation dynamics, heterogeneous electron transfer).

In the present work we will overview the results of a series of mixed quantum- classical molecular dynamics simulations, examine the physical properties of the hydrated electron in various environments and compare our results to available experimental data. The discussion will focus on the most critical issues and still unresolved questions about the basic aspects of the physics of these systems. In particular, we critically examine the traditional cavity model of the hydrated electron. The localization modes of the excess electron in water cluster anions and on water/air interfaces will also be discussed. Correlations of the localization of the excess electron with the size, internal energy, and the local molecular structure of the environment will be analyzed. We will also demonstrate the dramatic influence of the excess electron's state on the observable physical properties.

The work was supported by a grant to L. T. from the National Research Fund of Hungary (OTKA) under Contract K75285.

References

L. Turi, and Á. Madarász, Science 331, 1387 (2011). L. Turi, W.-S. Sheu, and P. J. Rossky, Science 309, 914 (2005). Á. Madarász, P. J. Rossky, and L. Turi, J. Chem. Phys. 130, 124319 (2009). Á. Madarász, P. J. Rossky, and L. Turi, J. Phys. Chem. A 114, 2331 (2010).

A Study of Allowed Electronic Transition of Organic liquid by using Attenuated Total Reflection in Far-Ultraviolet region. ~structure of liquid and electronic transition~

MORISAWA, Yusuke (Department of Chemistry, School of Science and Technology, Kwansei Gakuin University) ; IKEHATA, Akifumi (National Food Research Institute) ; GOTO, Takeyoshi (ational Food Research Institute) ; HIGASHI, Noboru (Kurabo Industries Ltd) ; OZAKI, Yukihiro (Department of Chemistry, School of Science and Technology, Kwansei Gakuin University)

Far-ultraviolet (FUV) spectroscopy revealed that the allowed electronic transitions of organic molecules. Because of large absorption cross section of these transitions, absorption spectra were investigated only in the gas phase. As to condensed phase, only few researches have been carried out, thus the absorption spectra in the condensed phase were not understood clearly. However such a strong absorption will be use in novel analytical method. We are developing an attenuated total reflection technique in the FUV region (ATR-FUV) to observe the strong allowed transitions of organic liquids. We investigated about basic organic solvent. We assigned absorption bands in the spectra to Rydberg transitions for these liquids. Several absorption bands were shifted by temperature, concentration of solution. In this presentation, several kinds of ketone, ether and alcohol were investigated. The ATR-FUV spectra of pure liquids and several kinds of solutions are measured. In order to assign the spectra, spectra in the liquid phase are compared with those in the gas phase. Ab- initio calculations at the EOM-CCS(D) and TD-DFT level for these molecules also compared with spectra in the liquid phase. We will discuss about the relation between structure of liquid and electronic transition.

Electrophoretic NMR - methodology and some applications

STILBS, Peter (Royal Institute of Technology (KTH))

Electrophoretic NMR (eNMR) is a technique with much unexploited potential in the field of Solution Chemistry. After several decades it now appears to become a standard tool, much complementing NMR diffusometry (PGSE-NMR, diffusion ordered NMR etc.), which has become widely used in later decades.

Electrophoretic NMR (eNMR), was visualized 40 years ago, but its robust practical implementation has developed slowly indeed. Here motion of ions or charged entities is detected by basically the same techniques used in NMR diffusometry (PGSE NMR, also often misleadingly called DOSY in later years) and in Magnetic Resonance Imaging (MRI, also named NMR microscopy for objects of a few cubic centimeters or less). Using a controlled magnetic field gradient across the sample, nuclei in different positions along the gradient will resonate at different NMR frequencies. Motion during the experiment can be detected by combining this position/magnetic field mapping with so-called spin-echo generation. These concepts are also old, and date back to the early days of NMR, more than 60 years ago. The aim of eNMR measurements is to simultaneously study the electrophoretic mobility of most or all of the charged entities in some solution system, normally an aqueous one. By combining information on their electrophoretic mobility with that from parallel measurements of their self- diffusion, one can also deduce the charge of the entities or ions in question, for example.

While PGSE NMR is widely used today, only a few groups have so far been successful in achieving any meaningful eNMR studies at all, or even a setup that works in principle. Main complicating factors are Joule heating of the sample, causing convective flow, and the parallel generation of electro-osmotic flow in the sample.

Also, combining the normal NMR experimental hardware with high-voltage components and metallic components in or near the detection region is problematic. The lecture will deal with some aspects of these matters, and report on some recent results on ion pairing in simple salts or ion binding in some polyelectrolyte-like systems of polymer-surfactant type. The following review articles[1-3] cover various aspects related to the contents of this lecture.

[1] M. Holz, Electrophoretic NChem.Soc.Rev. 23 (1994) 165-174 [2] C.S. Johnson, Jr. Electrophoretic Nin: D. M. Grant and R. K. Harris (Eds.), Encyclopedia of Nuclear Magnetic Resonance, Wiley, New York, 1996, pp. 1886-1895 [3] P.C. Griffiths Electrophoretic NMR - Ions, Molecules, Mixtures, Pores and Complexes., Annual Reports on NMR Spectroscopy, Vol 65, Chapter 5, (2009)

Accurate force fields from ab-initio simulations : The case of aqueous ions

ROTENBERG, Benjamin (CNRS et UPMC, Laboratoire PECSA) TAZI, Sami (UPMC) ; MOLINA, John (UPMC) ; SALANNE, Mathieu (UPMC)

The development of classical force fields for aqueous ions is a long-standing issue, due to their importance in many fields. Specific effects, i.e. the effect of the chemical nature of the ion, play an important role e.g. on DNA solvation [1] and on the sorption of ions onto mineral surfaces [2]. Molecular dynamics simulations are an effective tool in the analysis of the chemical and physical properties of solvated ions in solutions [3]. However, the reliability of their predictions depends on the quality of the force field used. We discuss here a method to derive a force field from ab-initio calculations, based on the "force- fitting" procedure [4]. Some of the parameters are fitted to ab-initio forces while others are directly calculated using maximally localized Wannier functions [5,6].

After describing the method, we illustrate its application to aqueous chloride, alkaline (Li+, Na+, K+, Rb+ and Cs+) and alkaline-earth (Mg2+, Ca2+ and Sr2+) ions. We validate the force field, by comparing its predictions to experimental structural (radial distribution function and EXAFS spectrum), dynamical (diffusion coefficient) and thermodynamical (Gibbs free energy of hydration) properties. Attention is also paid to ion-ion interactions so that the force fields are also able to reproduce crystalline structure of the corresponding series of chloride compounds.
References [1] Heyda et al, J. Phys. Chem. B 114, 1213 (2010) [2] Rotenberg et al, Geochim. Cosmochim. Acta 73, 4034 (2009) [3] Wernersson and Jungwirth, J. Chem. Theor. Comp. 6, 3233-3240 (2010) [4] Heaton et al, J. Phys. Chem. B 110, 11454 (2006) [5] Rotenberg et al, Phys. Rev. Lett. 104, 138301 (2010) [6] Molina et al, J. Chem. Phys. 134, 014511 (2011)

Multiscale modeling of ionic transport in charged clays

DUVAIL, Magali (Andra, 1 – 7 rue Jean Monnet, F-92298 Châtenay-Malabry, France and CNRS-UPMC, Laboratoire PECSA UMR 7195, 4 place Jussieu, F-75005 Paris, France) ; COELHO, Daniel (Andra, 1 – 7 rue Jean Monnet, F-92298 Châtenay-Malabry, France) ; BéKRI, Samir (IFP Energies nouvelles, 1 et 4 avenue du Bois-Préau, F-92852 Reuil-Malmaison, France) ; ROTENBERG, Benjamin (CNRS-UPMC, Laboratoire PECSA UMR 7195, 4 place Jussieu, F-75005 Paris, France)

We present a study of ionic transport through clays, in the context of the reversible geological disposal of radioactive waste. In many countries, clay formations are considered for this purpose because their properties (surface charge, low porosity) limit the diffusion and migration of ions in the environment. Predicting the long- term fate of radionuclides requires an understanding of transport processes in these multiscale materials. While transport on the microscopic (sub-nanometer) and macroscopic (multi-microns) scales are now well known, a lack remains in-between because there are currently no experimental techniques to probe the organization of the pore network on intermediate scales. We develop a model representing as accurately as possible the main macroscopic properties of a clay sample: porosity, pore radii, connectivity, ... taking into account the local transport properties of clays. We design a Pore Network Model (PNM), in which each pore is connected to others by channels, using experimental data. A Lattice-Electrokinetics scheme [1,2] is first used to model the microscopic transport properties through the interporal channels (nm scale). Then macroscopic properties (μm scale) are calculated from the microscopic ones using the PNM [3]. This coupled approach allows to address the key question: “How does macroscopic transport depend on small scale properties?”
References [1] B. Rotenberg, I. Pagonabarraga and D. Frenkel, Europhysics Letters 83, 34004 (2008). [2] B. Rotenberg, I. Pagonabarraga and D. Frenkel, Faraday Discussions 144, 233 (2010). [3] S. Bekri, C. Laroche and O. Vizika, Developments in Water Science 47, 1115 (2002).

Structural heterogeneity and anomalous hydrogen bonding in a series of primary alkylammonium nitrate ionic liquids revealed by High-energy X-ray diffraction experiments and MD simulations

SONG, Xuedan (Department of Chemistry, Faculty of Science, Kyushu University, Japan) ; HAMANO, Hiroshi (Department of Chemistry, Faculty of Science, Kyushu University, Japan) ; KANZAKI, Ryo (Graduate School of Science and Engineering, Kagoshima University, Japan) ; KAMEDA, Yasuo (Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Japan) ; KOHARA, Shinji (Japan Synchrotron Radiation Research Institute (JASRI)) ; FUJII, Kenta (Neutron Science Laboratory, Institute for Solid State Physics, The University of Tokyo, Japan) ; UMEBAYASHI, Yasuhiro (Department of Chemistry, Faculty of Science, Kyushu University, Japan)

Ethylammonium nitrate (EAN) is one of the most well known protic ionic liquids, which is expected as a proton conductive material for fuel cells due to low viscous and high ionic conductive properties. It is also demonstrated that EAN can be utilized as a solvent for self-assembles owing to hydrogen bonded network structure. Water like hydrogen bonded network structure of EAN play a key role in such applications. In addition, Atkin et al. found structural heterogeneity of liquid EAN, though it has a quite short ethyl chain [1]. We revealed the significant structural correlation among the terminal methyl groups of EAN [2]. Recently, Hayes et al. performed neutron diffraction experiments with the H/D isotopic substitution techniques to probe structural heterogeneity of EAN [3]. However, molecular origin of structural heterogeneity of EAN is unclear yet.

We investigated liquid structure of a series of primary alkylammonium nitrate with varying alkyl chain lengths from 2 to 4 by high-energy X-ray diffraction experiments with the aid of MD simulations to reveal molecular origin of structural heterogeneity. The characteristic peak in the low-Q range can be attributable to the anion-anion long-range correlations, which is excluded by the aggregated alkyl chains of the primary ammonium. In addition, we found remarkably distorted NH...O hydrogen bonding between cation and anion in the ionic liquids, though it is close to linear in the optimized geometry by ab initio calculations in gas phase.

1.Atkin, R.; Warr, G. J. Phys. Chem. B 2008, 112, 4164. 2.Umebayashi, Y.; Chung, W.; Mitsugi, T.; Fukuda, S.; Takeuchi, M.; Fujii, K.; Takamuku, T.; Kanzaki, R.; Ishiguro, S. J. Comput. Chem. Jpn. 2008, 7, 125 3.Hayes, R.; Imberti, S.; Warr, G. G.; Atkin, R. Phys. Chem. Chem. Phys. 2011, 13, 3237.

Efficient gold extraction from water by use of ionic liquids

VITE, Ghislain (Université de Savoie - LCME) ; PAPAICONOMOU, Nicolas (Université de Savoie - LCME) ; LéVêQUE, Jean-marc (LCME - Université de Savoie) ; BILLARD, Isabelle (CNRS-IPHC/DRS UMR 7178)

Industrial recovery of gold from ores involves in most cases cyanidation of oxydized gold (AuI or AuIII) which has well-known environmental issues.[1] Gold is also a precious metal present in all electronic wastes, in most connectors for instance and its recovery is also of environmental concern.

Alternative strategies to provide more environment-friendly processes for refining and recycling gold involve the oxydation of metallic gold to AuIII, with oxygen for instance, and subsequent dissolution in water as tetrahalogenaoaurate (AuX4-, where X stands for Cl- or Br-) anion, using hydrochloric or hydrobromic acid.[2] Because ionic liquids (ILs) are non flammable, exhibit high thermal stability and mostly now various pressure[3], they are promising candidates for the extraction of hydrophilic tetrahalogenoaurate anions from water. We present two ways to recover efficiently gold from acidic aqueous solutions, based either on gold precipitation, with use of water-soluble ILs, or on gold extraction towards pure hydrophobic IL phases. In both cases, ionic liquids based on 1-methyl-3-octylimidazolium [OMIM], 1-octylpyridinium [OPYR] or 1-methyl-1-octylpyrrolidinium [MOPYRRO] cations were used. Two types of anions were used, namely halides (Cl- or Br-) and bis(trifluoromethanesulfonyl)imide (NTf2-) which allowed us to easily switch from precipitation to liquid/liquid extraction. Precipitation of tetrahalogenoaurate anions from acidic aqueous phases (pH = 1 to 4, using HCl or HBr) was obtained by adding KAuX4 with [OMIM][Cl], [OMIM][Br], [OPYR][Br] or [MOPYRRO][Br], accordingly. In all cases, precipitation occurred within a few hours. The precipitate was expected to correspond to the formation of hydrophobic [OMIM][AuX4], [OPYR][AuX4] or [MOPYRRO][AuX4] salts. Following this assumption, solubility products for all salts were calculated and ranged between 10^-5 and 10^-6. All of the precipitates were found to be solid at room temperature, except for [OMIM][AuCl4]. The latter salt can therefore be considered as a room temperature ionic liquid. Extraction of tetrahalogenoaurate anions from the same acidic water phases was performed with [OMIM][NTf2], [OMIM][NTf2] and [OMIM][NTf2]. [OMIM][NTf2] appeared to be the most efficient IL, exhibiting distribution coefficients D above 10 000. The UV-Vis spectra recorded for the gold complex in the ionic liquids revealed a systematic shift of 20 nm for the absorption bands of AuCl4^- and AuBr4^-. This could result from the formation of a new gold complex of the type AuX5- or AuX6- within the ionic liquid phase, or from the presence of cations [OMIM], [OPYR] or [MOPYRRO] in a second coordination sphere around the gold complex. These results suggest that ionic liquids can be successfully applied to the recovery of gold from water. Both methods proposed here, namely precipitation or extraction, have the advantage to provide safe and environmental-friendly alternatives to current gold recovery processes. Considering the lower cost of halide-based ionic liquids a compared to hydrophobic NTf2-based ionic liquids, precipitation appears to be a cheaper process. Besides, contacting hydrophobic ionic liquids with water always results in a loss of some of the ionic liquid in the aqueous phase. However, extraction of anionic gold complex with hydrophobic ionic liquids allows the recovery of gold from direct electrodeposition within the ionic liquid. Further studies include fundamental studies of the stoichiometry of gold-halide complexes within ionic liquids, and competitive extraction of gold complexes in presence of other metals such as silver or copper, which occur in both ores and electronic wastes. Besides, such a strategy to extract metallic anions by using ionic liquids can be extended to the extraction from water of other metals such as molybdenum, tungsten and vanadium.

References 1. http://www.infomine.com/publications/docs/Miranda2010.pdf http://www.cyanidecode.org/cyanide_environmental.php 2. Usher, A., McPhail, D.C. and Brugger, J. (2009) A spectrophotometric study of aqueous Au(III)-halide-hydroxy complexes at 25°C. Geochimica et Cosmochimica Acta, 73, 3359-3380. 3. K. Seddon. The handbook of ionic liquids: synthesis and characterization , Wiley-Interscience, 2011.

Thermodynamic peculiarities and phase diagrams of quaternary solutions with chemical reactions and miscibility gap: critical states, phase and chemical equilibria

TOIKKA, Maria (Department of Chemical Thermodynamics and Kinetics, Faculty of Chemistry, Saint-Petersburg State University, Universitetsky prospect 26, Peterhof, Saint-Petersburg, 198504, Russia)

The simultaneous phase and chemical processes is of great importance both for basic research and for chemical engineering, e.g. chemical process design. The chemical reaction processes are limited by chemical equilibrium (CE) between reactants and products, so many industrially important chemical processes must include following separation of equilibrium mixture and recycling of the reactants. Also the limited miscibility in reacting mixture may substantially influence on chemical reaction and complicate the industrial process. New ideas and problems of such coupled processes had determined the development of thermodynamic theory of complex systems. Generally these researches are theoretical and concerned with reactive distillation, i,e. coupled distillation and reaction process [1]. In our work we carried out the experimental and theoretical study of phase behavior of the systems with chemical reaction in solution. The main objects are quaternary systems with ester synthesis reaction. The aim of the paper is to consider some theoretical and experimental results on the thermodynamic peculiarities and phase diagrams of the systems with chemical reactions in solution with miscibility gap. In spite of the large variety of available data on solubility and liquid-liquid equilibria (LLE) in fluid systems only limited number of these works is devoted to the thermodynamic study of the solution with simultaneous CE and LLE (e.g. see [2, 3]). The experimental database on LLE in solution with CE and nonequilibrium chemical reactions is relatively poor in general. Chemical reactions in solutions with limited miscibility lead to new singularities of phase diagrams and significantly influence on the run of liquid-liquid phase transitions. In this paper we present the brief review and discussion of the new data on phase diagrams of quaternary systems with ester synthesis reaction. On the base of new experimental results we consider some thermodynamic aspects of the behavior of quaternary reacting systems with liquid splitting. Cases of equilibrium and nonequilibrium chemical reactions in the immiscibility region are presented for the systems with ethyl acetate and n-propyl acetate synthesis reactions. The phase diagrams in the case of simultaneous LLE and CE are considered on the example of acetic acid – n-propanol – n-propyl acetate – water systems. Such simultaneous equilibrium means intersection of CE and binodal surface in composition tetrahedron of quaternary system. The composition area of simultaneous LLE and chemical equilibrium should be considered as analogous to unique reactive tie-lines in ternary systems [2]. Some possible topological structure of diagrams for the solutions with miscibility gap and CE (also nonequilibrium reaction) are discussed. The critical states of LLE in the case of miscibility gap are an obligatory aspect of thermodynamic consideration. In the case of quaternary LLE at isothermal-isobaric conditions the critical states belongs to the curve in composition tetrahedron: such critical curve is formed by the set of critical points on the binodal surface. In general the critical curve belongs to chemically equilibrium and nonequilibrium area of phase diagram. The intersection of CE and binodal surface leads to the appearance of unique chemically equilibrium critical points. We consider such critical points and their temperature shifting on the base of our experimental data. The possible transformations of the topological structure of diagrams of quaternary reactive systems with critical points of LLE are discussed on the base of thermodynamic approach.

The complex structure of solution in the case of the splitting and the chemical reaction is a main factor that should be taken into account in the liquid reaction extraction process design. For example, the shift of the solution composition due to the chemical reaction can lead to considerable experimental errors in the determination of phase equilibrium parameters. Unfortunately the existing experimental data base on reacting systems with miscibility gap is very limited still and needs in further development.

Acknowledgment Author acknowledge Saint-Petersburg State University for the research grant (reg. No 12.0.105.2010 (01201052803)) and financial support (reg. No 12.41.417.2011).

References 1. K. Sundmacher and A. Kienle A. (Eds.) Reactive Distillation – Status and Future Directions, Wiley-VCH. Weinheim. (2003). 2. S. Ung, M. Doherty. Chem Eng. Sci. 50, 3201 (1995). 3. A. Toikka, M. Toikka. Pure Appl. Chem., 81, 1591 (2009).

Structure and dynamics of a lithium ion in ionic liquids: toward high safety batteries.

UMEBAYASHI, Yasuhiro (Kyushu University)

Not only the global environmental concerns but also recent Japanese disaster of earthquake and tsunami followed by serious power supply insufficiency caused by terrible damage of nuclear power plants, it is urgent problem to realize ubiquitous high energy-density power storages with high safety such as batteries, capacitors and fuel cells. How can we solution chemists contribute? One of the solutions may be to clarify what is happening in solutions.

As is well recognized, lithium ions are one of the key materials to achieve such high energy-density batteries. In this context, non-aqueous lithium salt solutions are actually ubiquitous, because they used in batteries for our mobile PCs and cellular phones. We solution chemists have so far endeavor to reveal structure and dynamics of lithium ion in aqueous and non-aqueous solutions, so that the fundamental knowledge has accumulated until now. However, it is still needed to reduce risks of spontaneous combustion or explosion of lithium salts in non-aqueous solutions. Recently, entirely new solvents were discovered; Room Temperature Ionic Liquids. Negligible vapor pressure, thus practically non-inflammability of these materials is a favorable nature to apply them to solvents for a lithium conductive electrolyte. In this contribution, our recent works will be shown; i.e., structure and dynamics of a lithium ion in ionic liquids by means of Raman spectroscopy and quantum chemical calculations, and high-energy X-ray diffraction with the aid of MD simulations. Thus, we solution chemists can provide the fundamental knowledge on a metal ion in solutions, which can be a good guide for researchers to develop their materials in a wide field of applications.

References 1. Umebayashi, Y.; M. Mitsugi,; Fukuda, S.; Fujimori, T.; Fujii, K.; Kanzaki, R.; Takeuchi, M.; Ishiguro, S., J. Phys. Chem. B, 2007, 111, 13028-13032. 2. Shirai, A.; Fujii, K.; Umebayashi, Y.; Ishiguro, S. Ikeda, Y., Anal. Sci., 2008, 24, 1291-1296. 3. Umebayashi, Y.; Mori, S.; Fujii, K.; Tsuzuki, S.; Seki, S.; Hayamizu, K.; Ishiguro, S., J. Phys. Chem. B, 2010, 114, 6513-6521.

Use of microcalorimetry to determine the enthalpies of solid-solution exchanges

MOREL-DESROSIERS, Nicole (Université Blaise Pascal, LMGE, UMR UBP-CNRS 6023)

Sorption processes may be affected by temperature and this may be of prime importance in some cases. This is particularly true in the context of radioactive waste disposal in underground repositories. In order to have a complete thermodynamic description of a sorption process, it is thus necessary to go beyond the commonly used distribution coefficient Kd by looking at the enthalpy of solid-solution exchange. However, whereas the equilibrium constants for the ion exchange reactions of several materials were measured under various conditions, it appears that the enthalpies were only scarcely determined. Furthermore, most of these enthalpies were indirectly obtained through van't Hoff plots. This lack of direct experimental data may be explained by the difficulties encountered for such determinations. The measurement of the heat effect associated with an exchange process between a solution and a solid can only be carried out with a sensitive microcalorimeter designed for the monitoring of slow processes. This cannot be routine work since a specific experimental protocol has to be designed for each type of system studied. Some examples will be shown here for the ion exchange in natural and synthetic clays, the sorption of ions on alumina, and the hydration of montmorillonite.

Sharp decrease of the dielectric friction on polyions during conformation transition from pearl-chain to coiled shapes

M'HALLA Jalel, BOUGHAMMOURA Sondès, GHAZOUANI Anis.
Faculty of Sciences, UR « Electrolytes », University of Monastir, 5000 Monastir, Tunisia.

It was generally assumed that, at low concentration C_P, the repulsion between charged monomers prevents the collapse of the long chain of a polyion. However, continuous transition from stretched form to coiled shape could be observed by increasing the concentration C_i of counterions or by decreasing the permittivity ε of the solvent.

In this contribution, we show that the generalization of the classic Zwanzig's theory for spherical ions to polyions, predicts that this conformation transition is accompanied by a sharp decrease of the translational dielectric friction on the polyion.

The coiled polyion of structural charge Z_Se and structural volume V_P, is treated as a uniformly charged rigid ellipsoid of O center, A, B focuses, L length = AB, R minor axe and a_R major axe. The general expression of the degree of the ionic condensation ($1-\alpha_c$) in terms of the "conformation function" g(x,L) and the Debye-MSA screen parameter Γ is:

$$[(1-\alpha_c)/(\alpha_c)][1-V_PC_P] = V_PC_P[g(R,L)/g(d,L)]^{[b''(\alpha_c+|Z_i/Z_S|)]}$$

$$g(x,L) = [(4x^2+L^2)^{1/2}+L]/[(4x^2+L^2)^{1/2}-L] \; ; \; b'' = |Z_i|(L_B/b_S) \; ; \; b_S = L/|Z_S| \; ; \; L_B = e^2/(\varepsilon kT)$$

$$d = R + 1/2\Gamma \; ; \; \Gamma^2 = \pi L_B Z_i^2(\alpha_c C_i)[1+2\Gamma R_i]^{-2}$$

α_c verifies the Ostwald's principle of dilution: ($\alpha_c \rightarrow 1$ when the ionic concentration $C_i \rightarrow 0$).

The expression of the effective mobility u_{eff} of the polyion submitted to an external field E is:

$\mathbf{u_{eff} = |(\alpha_c Z_S e)/6\pi\eta C_{ap}'|(1+\beta'_{ir}+\beta'_{df})^{-1}}$

η is the viscosity of water, C_{ap}' is the "Gouy capacitance" (in c.g.s.u.e units) of the ellipsoidal capacitor constituted by the polyion and its ionic atmosphere. The term $\beta'_{ir} \equiv |\Delta X_{ir}/E|$, expresses the ionic relaxation effect:

$\mathbf{\beta'_{ir} = (\alpha_c)|Z_i Z_S|(L_B/18d)(3+\gamma_d^2)(1+\gamma_d^2)^{-3/2}}$ **with:** $\mathbf{\gamma_d = (L/2d)}$

The term $\beta'_{df} \equiv |\Delta X_{df}/E|$, expresses the dielectric frictional force $\mathbf{F_{df} = (\alpha_c Z_S e)\Delta X_{df}}$, and:

$\mathbf{\beta'_{df} = (2/3)|(\alpha_c)Z_S|^2(1-\varepsilon.\varepsilon_0^{-1})(R_w/R_{app})^3(L_B/C_{ap}')}$; $\mathbf{C_{ap}' \leq R_{app}(\gamma) \leq L/2}$; $\mathbf{\gamma = (L/2R)}$

R_w is the radius of a water molecule and R_{app} is the apparent radius of the polyion.

For a stretched polyion (Pearl-chain), we substitute L by its structural length L_S, and β'_{df} by:

$\mathbf{\beta'_{df,PC} \approx (2/3)(\alpha_c)^2(1-\varepsilon.\varepsilon_0^{-1})(R_w/b_S)^3(L_B/C_{ap}')|(f^3-4.808)|Z_s|+6.58|}$; $\mathbf{f = b_S/R_g \geq 2.}$

R_g is the radius of the charged monomer (pearl); therefore the decrease of the dielectric friction is given by the ratio: $(\beta'_{df}/\beta'_{df,PC}) << 1$.

$\mathbf{\beta'_{df}/\beta'_{df,PC} \approx (1/3)|Z_s|(b_S/R_{app})^3}$; which is of about : $(\pi/|Z_s|)^2$, for $R_{app} \approx L_S/\pi$

These results are illustrated by some conductivity measurements of some polyelectrolytes.

Acid solubilisation into hydrophobic ionic liquids: role of TBP co-solvent investigated by experiments and simulation

GAILLARD, Clotilde (IPNL - CNRS) ; MAZAN, Valérie (IPHC - CNRS) ; GEORG, Sylvia (IPHC - CNRS) ; KLIMCHUK, Olga (IPHC - CNRS) ; BILLARD, Isabelle (IPHC - CNRS)

Room temperature ionic liquids (RTIL) are solvents composed only of ionic species, typically of a small inorganic anion and a large organic cation. In general, they exhibit a negligible vapour pressure at room temperature and good solvating properties for ionic and molecular compounds that render them suitable for a wide range of applications. One of the possible uses of hydrophobic IL is for liquid- liquid extraction. Extraction mechanisms in ionic liquids are shown to be complex as they strongly depend on the IL nature (in particular the alkyl chain length, for example see [1]) but also on the aqueous phase composition. In particular, the presence of "spectator" ions may interfere, causing either "salting-out" or "salting-in" effects, changing the mutual solubility of the solvents [2] and subsequently, extraction coefficients.

As a consequence, we have carried out a work aiming at characterizing the acid solubilisation from an aqueous phase to an ionic liquid phase composed of BMITf2N, containing or not TBP. Four different acids are investigated: HNO3, HCl, HReO4 and HClO4, in a wide range of concentration (from 0 to 6-7 M). The effect of tributylphosphate (TBP) as co-solvent of the IL phase is investigated. This molecule is used to separate uranium (as a complex of TBP and nitrate ions) during the nuclear fuel reprocessing.

Acid solubilisation is found to be negligible for all acids excepting for HNO3 when its initial aqueous concentration is above 3 M. We have also followed the evolution of the mutual solubility of water and IL, which is shown to depend on the TBP presence and on the nature of the acid. Molecular dynamics simulations confirm this result evidencing that the nitric acid is extracted as the non-dissociated HNO3. During extraction, TBP plays an important role on the mutual solubility between water and ionic liquid, enhancing the exchanges between those two solvents.

[1] M. L. Dietz, D. C. Stepinski Talanta. 2008, 75, 598. [2] J. R. Trindade, Z. P. Visak, M. Blesic, I. M. Marrucho, J. A. P. Coutinho, J. N. C. Lopes, L. P. N. Rebelo J. Phys. Chem. B. 2007, 111, 4737.

Structure, properties of water and new approaches to assessment of drinking water quality

GONCHARUK, Vladyslav (Academician-Secretary (Head) of Chemistry Division of National Academy of Sciences of Ukraine, Director of the A.V.Dumansky Institute of Colloid and Water Chemistry of the NAS of Ukraine)

The uniqueness of properties of water, which we used to consider as the most simple and investigated compound, is determined by its isotopic composition, and above all by protium and deuterium ratio. Data on physicochemical properties of the light water (the ratio D/H = 4 ppm and 18O/16O = 750 ppm) have been obtained. In terms of a series of physicochemical properties the light water is a new associated liquid that is insufficiently known earlier. It is given explanation for the determined significant changes of properties of the light water in comparison with the high- resistance water of natural isotope composition, which is based on mechanism of formation of supramolecular density inhomogeneities – deuterium-stabilized heterophase clusters. It is shown that biological effects of the light water are not related to the ligand dependent toxic effect, but determined by the adaptive reasons. The modern, extremely critical situation with the quality of drinking water have been analyzed. It was substantiated the inconsistency of existing approaches to the assessment of drinking water quality and the necessity of introducing a new concept of drinking water standards. The fundamentally new approaches to the assessment of its quality have been set out. The new State Standard of Ukraine for drinking water, whose legalization will make it possible to provide the population with drinking water—biologically and physiologically safe for human organism, is presented.

Behavior of hydrophobic ions in aqueous medium

BHOWMIK, Debsindhu (Laboratoire Léon Brillouin, UMR CEA-CNRS 12, CEA Saclay, 91191, Gif-sur-Yvette, France) ; MALIKOVA, Natalie (Laboratoire Léon Brillouin, UMR CEA-CNRS 12, CEA Saclay, 91191, Gif-sur-Yvette, France) ; TEIXEIRA, José (Laboratoire Léon Brillouin, UMR CEA-CNRS 12, CEA Saclay, 91191, Gif-sur-Yvette, France) ; MÉRIGUET, Guillaume (Université Pierre et Marie Curie-Paris 6, UMR-UPMC-CNRS-ESPCI 7195, Laboratoire PECSA, Case 51, 4 place Jussieu, Paris F-75005, France) ; BERNARD, Olivier (Université Pierre et Marie Curie-Paris 6, UMR-UPMC-CNRS-ESPCI 7195, Laboratoire PECSA, Case 51, 4 place Jussieu, Paris F-75005, France) ; TURQ, Pierre (Université Pierre et Marie Curie-Paris 6, UMR-UPMC-CNRS-ESPCI 7195, Laboratoire PECSA, Case 51, 4 place Jussieu, Paris F-75005, France)

The main objective of this work is to investigate solute and solvent dynamics in hydrophobic charged systems. Tetra-alkyl ammonium (TAA) (TMA=tetra-methylammonium, TBA=tetra-butylammonium) ions are considered to be good model by providing a competing force of hydrophobic effect and electrostatic interaction. Though their macro and microscopic properties are being investigated for long by different experimental and simulation techniques [1], the molecular basis and combination of electrostatic and hydrophobic interaction is yet to be properly understood. There exist some studies on TAA ion dynamics but without much detail of different spatial and temporal scale [2]. Structural analysis suggests that solvent is not significantly different from bulk water [1] though origin of its slow dynamics is inconclusive [2] [3]. For highly concentrated TAA solutions, we take advantage of Quasi Elastic Neutron Scattering (TOF and NSE) techniques coupled with all-atom explicit molecular dynamic (MD) simulation to explore solute and solvent dynamics, the structure is studied by a combination of Small Angle Neutron scattering, Diffraction and MD. We present in particular a detailed structural and dynamical analysis of aqueous TBABr solutions in comparison to NaBr, TMABr, CholineBr at different concentrations and temperatures. In case of 1m (molar) TBABr, anion and water molecules can penetrate into hydrocarbon chains which remain stretched (~93%) and repulsion between cations is significantly nullified. We will find out why cation translational diffusion coefficient ('D') extracted from by incoherent and coherent neutron scattering signal, estimates different values. At this concentration TBA dynamics is ~20 times slower than bulk water. Contrary to previous results [2] we will see that its translational diffusion is accompanied by global and methyl group rotation. The activation energy associated with coherent signal is significantly higher (~1.4 times) than bulk water and 3 times higher than the energy of an H-bond. For TBA, hydration shell is less defined compared to other cations and solvent 'D' is reduced by a factor of ~2 while for TMA, choline or Na, this factor is ~1.4.

[1] Barthel J., J. Sol. Chem. 1994, 23, 9; Kunz W., J. Chem. Phys. 1990, 92, 4; Turner J. et al, J. Chem. Phys. 1994, 101, 6116; 1995 102 (13) [2] Novikov A. G. et al, J. Mol. Liquids 79 1999, 437; Novikov A. G. et al J. Mol. Liquids 2001 91; Hertz H. G. et al Berichtc der Bunscngescllschaft 1969 73 (6) [3] Calandrini V. et al, Appl. Phys. A [Suppl.] 2002, S1339-S1341C; Bhowmik D. et al, submitted

Diffusion and partitioning of some organic molecules and ions in aqueous micellar solutions

TOMINAGA, Toshihiro (Okayama University of Science)

We have measured limiting interdiffusion coefficients for electron-acceptor ions such as a series of dialkylviologen cations$^{1)}$ and quinone sulfonate anions in cationic and anionic micellar solutions. We have also made the measurements for phenylalkanols in micellar solutions of a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB).$^{2)}$ We have extended the measurements in solutions of another cationic micelles such as dodecyltrimethylammonium bromides (DTAB) and hexadecyltrimethyl- ammonium bromides (CTAB), anionic micelles such as sodium dodecyl sulfate (SDS), and zwitterionic micelles such as N-dodecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (DDAPS) and N-tetradecyl-N,N-dimethyl-3-ammonio-1-propane sulfonate (TDAPS).

From the diffusion coefficients in water, the effect of hydration for the diffusion of these ions and molecules are discussed. Values for the degree of association of the probe species to the miclles, p, were determined by

$$D_{obs} = (1-p)D_w + pD_m \qquad (1)$$

where D_{obs} and D_w are diffusion coefficients of the probe species in micellar solutions and water, respectively and D_m is the tracer diffusion coefficient of a given micelle, which was obtained by measuring the diffusion coefficient of pyrene solubilized in the micelle. From the p values we calculated partition coefficients of the probe species between micellar pseudophase and bulk aqueous phase, $K_x = x_m/x_w$, where x_m and x_w are mole fractions of the probe species in micellar pseudophase and bulk aqueous phase, respectively.

For phenylalkanols, effects of the chain-length of both penylalkanols and surfactants on the K_x values are discussed. Effects of the surfactant head-groups on the K_x values are also discussed.

References

T. Tominaga, H. Ohtaka-Saiki, Y. Nogami, H Iwata, *J. Mol. Liq.*, **125**, 147-150 (2006).
T. Toki, T. Shimeno, T. Tominaga, *J. Chem. Eng. Data*, **55**, 2017-2020 (2010).

Mesoscopic structures induced by the solvation effect of antagonistic salts in the mixture of water / organic solvent

SADAKANE, Koichiro (High Energy Accelerator Research Organization) ; NAGAO, Michihiro (NIST Center for Neutron Research, National Institute of Standards and Technology) ; ENDO, Hitoshi (Jpan Atomic Energy Agency) ; SETO, Hideki (High Energy Accelerator Research Organization)

The structure and dynamics of a ternary system composed of deuterium oxide, 3-methylpyridine (or 2,6-Lutidine), and an antagonistic salt (e.g., sodium tetraphenylborate) are investigated by means of small-angle neutron scattering and neutron spin echo. The results showed that the highly-ordered structures, such as a multi-lamellar vesicles, are induced due to the effect of salts.

Possible routes for pyrochemical separation

DELPECH, Sylvie (CNRS) JASKIEROWICZ, Sébastien (CNRS) ; SLIM, Cyrine (ENSCP)

Molten salts such as chloride or fluoride salts at high temperature (400-800°C) are solvents known for their high solvation power and their high electroactivity range. Rare earths, lanthanides, actinides, refractory metals can be dissolved, treated, purified in molten salts.

The pyrochemical separation and extraction of solutes can be performed using several methods taking into account the effects of redox and/or acidity. Thus, some methods are based on modifications of oxidation states of the elements considered either by the action of selected oxidizing or reducing reagents or by the use of an electrical current. In some cases, the oxidation leads to the formation of a gaseous compound. The reduction reaction generally leads to the formation of a metal or an alloy.

Metals are obtained by electrochemical reduction on solid and inert cathodes. Reduction can also be performed on a liquid cathode, so called solvent metal (e.g. Bi, Ga, Sb, Cd, Al...), either by electrochemical reduction or by chemical reaction with a reducing reagent (such as Li or Th), solvated in the liquid metal solvent. In this latter case, the product of the reduction is a metal solvated by the liquid solvent metal. Other methods use the oxoacido-basic properties (oxide anion exchange power) of the solutes. The control of the amount of oxide ions in melt can lead to a selective precipitation of an oxide which can be subsequently separated from the liquid media. All these technique can be studied using an analytical approach based on both thermochemical and experimental analysis. The objective of this talk is to present our analytical approach through two examples of pyrochemical separation: the oxide precipitation and the reductive extraction.

Conductivity of electrolyte solutions-an outdated story ?

BESTER ROGAC, Marija (University of Ljubljana)

The temperature and concentration dependence of the electrical conductivity of electrolyte solutions has been proved as one of the most appropriate methods for studying ion-ion, ion-solvent and solvent-solvent interactions in solutions since the beginning of the 20th century. Significant progress has been made during last decades when high accuracy in conductivity measurements over a sufficiently large temperature range provided reliable conductivity data for evaluation within the framework of modern electrolyte theories. Nevertheless, at present, the electrolyte conductivity measurement is often treated as an old-fashioned method.

In this contribution a short review of an actual state of knowledge on electrolyte solutions will be given. More attention will be dedicated to the low concentration chemical model (lcCM) which turned out as very successful for the analysis of the association processes of symmetrical electrolytes in aqueous and non aqueous solutions. Some results, obtained by the analysis of electrical conductivity data for some simple electrolytes (in water and water-1,4-dioxane mixtures) [1-3], some drugs [4,5], ionic liquids [6,7], and hydrophobic ions (represented by tetraalkylammonium salts of cyclohexylsulfamic acid) [8] in aqueous solutions will be presented. As expected, in all these electrolyte solutions in water the ion association is relatively weak, but sometimes perceivable and strongly dependent on the cation-anion combination. It could be assumed that the ion pair formation is more expressed if the hydration of cation and anion is similar. In the mixed solvents the ion association is increasing with the decreasing relative permittivity of the mixture. According to their structure, ionic surfactants belong also to the electrolytes, but here lcCM can be applied below critical micelle concentration only. However, mean sphere approximation (MSA) can correctly reproduce experimental conductivity data below and above critical micelle concentration and also calculate the effective charge of the micelles [9].

Thus, electrolyte conductivity still provides very important information about the properties of electrolyte solutions. With the help of contemporary equipment the determination of precise temperature-dependent electric conductivity data nowadays is more user-friendly what makes this method interesting and appealing again. But there are still challenges in developing fundamental models which would take into account the actual species present and their variation with the overall electrolyte concentration.

1. M. Bešter-Rogač, R. Neueder, J. Barthel, J. Solution Chem. 1999, 28, 1071. 2. M. Tomšič, M. Bešter-Rogač, A. Jamnik, R. Neueder, J. Barthel, J. Solution Chem. 2002, 31, 19. 3. M. Bešter-Rogač, N. Hauptman, J. Barthel, J. Mol. Liq. 2007, 131-132, 29-35. 4. M. Bešter-Rogač, Acta Chim. Slov. 2009, 56, 70. 5. M. Bešter-Rogač, M. Bončina, Y. Apelblat, A. Apelblat, J. Phys. Chem. B. 2007, 111, 11957. 6. M. Bešter-Rogač, J. Hunger, A. Stoppa, R. Buchner, J. Chem. Eng. Data 2010, 55, 1799. 7. M. Bešter-Rogač, J. Hunger, A. Stoppa, R. Buchner, J. Chem. Eng. Data 2011, 56, 1261. 8. M. Bešter-Rogač, C. Klofutar, D. Rudan-Tasic, J. Mol. Liq. 2010, 156, 82. 9. G. M. Roger, S. Durand-Vidal, O. Bernard, P. Turq, T.-M. Perger, M. Bešter- Rogač, J. Phys. Chem. B 2008, 112, 16529.

Effect of glucose on the volumetric behavior of some amino acids in aqueous media at different temperatures

JAMAL, Muhammad Asghar (Government College University Faisalabad) ; KHOSA, Muhammad Kaleem (Government College University Faisalabad), HANIF, Tosif (Government College University Faisalabad) ; SHAZAD, Khurram (Government College University Faisalabad)

Densities and sound velocities of glycine, and methionine in aqueous glucose solutions have been measured at T=298.15, 303.15, 308.15 and 313.15 K by an Anton Paar density sound analyzer (DSA 5000). This data have been used to calculate apparent molar volumes, Vf, partial molar volume, V0, and partial molar compressibility, φk. The negative values of partial molar compressibility with rise in temperature were observed which The values of φk are negative for all the three amino acids in aqueous glucose solutions, indicating that the water molecules around ionic charged groups of amino acids are less compressible than the water molecules in the bulk solution and hence indicate smaller solute-solvent interactions caused by electrostriction of water molecules. All transfer values are found to be negative which have been discussed in terms of the interactions between ions (charged centers), hydrophilic groups (OH and CONH) and hydrophobic groups.

Lewis basicity scales in liquids from first-principles

SALANNE, Mathieu (Université Pierre et Marie Curie)

In liquids, a measure of the Lewis basicity of a solvent is commonly provided by the optical basicity, i.e. the ability of the solvent molecules to donate their electrons to an acidic species. This quantity is known to vary with the polarizability of the Lewis base, which reflects the susceptibility to distorsion of its electronic cloud in a given environment.

In this study, individual molecular polarizabilities were computed from first- principles for a series of liquids, ranging from protic solvents (pure water, hydrogen fluoride, ammonia and their mixtures) to high temperature ionic liquids (molten fluorides, magmatic melts). From these calculations optical basicity scales were set up for each Lewis base, in which any material can be classified unambiguously.

In protic solvents, we show that the optical basicity scale correlates well with the corresponding scale obtained within the commonly used Bro nsted-Lowry definition of acidity. This allows us to propose a simple yet accurate method for determining the acidity of protic solvents. We illustrate this method with the example of a room temperature ionic liquid, NH4F-2.2HF. The predicted value for the acidity of this solvent is in excellent agreement with the results obtained using an ab initio molecular dynamics approach.

References: 1 M. Salanne, R. Vuilleumier, P. A. Madden, C. Simon, P. Turq and B. Guillot, J. Phys.: Condens. Matter, 2008, 20, 494207 2 M. Salanne, C. Simon, P. A. Madden, Phys. Chem. Chem. Phys., 2011, 13, 6305

Time evaluation of aqueous leachates composition from pyrite and gossan wastes amended with organic and inorganic materials. Pot experiments

ABREU,Maria Manuela (Unidade de Investigação de Química Ambiental, Instituto Superior de Agronomia, TU Lisbon, Tapada da Ajuda, 1349-017 Lisboa, Portugal) ; SANTOS, Erika (Centro de Investigação em Ciências do Ambiente e Empresariais, Instituto Superior D. Afonso III, Convento Espírito Santo, 8100-641 Loulé, Portugal) : MAGALHãES, Maria Clara (Departamento de Química e CICECO, Universidade de Aveiro, Aveiro, Portugal) ; MACIAS, Felipe (Departamento de Edafología y Química Agrícola, Facultad de Biología, Universidad de Santiago de Compostela, Campus Universitario Sur, 15782 Santiago de Compostela, Spain)

Metal mining in the massive sulfides from São Domingos (Iberian Pyrite Belt, SE Portugal) generated large volumes of tailings, composed of different types of waste materials, as *gossan*, host rocks, roman and modern slags, smelting ashes, and brittle and blocks of pyrite most of them unable to support plants due to their characteristics. The sulfide containing tailings are mainly characterized by continuous generation of acid drainage and dispersion of chemical elements in the environment.

Composite samples of two different mining wastes (1-gossan materials; 2-crushed pyrite+smelting ashes) from São Domingos mine area were amended with mixtures (150 Mg/ha) of rockwool (RW), two agriculture wastes (AW) and wastes from *Arbutus unedo* (ArbW) fruits liquor distillation. Two treatments are being carried out (control, RW+AW+ArbW) in pots, in triplicate, under controlled conditions in greenhouse, for almost one year, with leachates collected after one, four and seven months of incubation. Limestone rock wastes were only added, at 55 Mg/ha, to pyrite materials to increase pH for similar values of *gossan*. Crushed pyrite+smelting ashes presented pH~2, and large total concentrations (g/kg) of Al (58.1), As (1.1), Cu (2.1), Fe (107.3), Pb (11.7), S (65.3) and Zn (1.1). *Gossan* materials with pH~4 also present high concentrations (g/kg) of Al (24.8), As (3.0), Cu (0.2), Fe (129), Pb (9.2) and S (13.7).

The experimental values obtained for the concentrations of the above referred chemical elements as well as the pH of the leachates after one month (experiments with number 1), four months (experiments with number 4), and seven months of incubation (experiments with number 7) are presented in the Table 1.

Table 1. - Time variation of pH and chemical elements concentrations in leachates after one month (1), four months (4) and seven months (7)

Experiment	pH	sulfate (g/L)	Al (mg/L)	As (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Zn (mg/L)
				Gossan				
Control-1	4.0	0.171	2.96	7.3×10^{-4}	0.49	0.52	0.54	0.08
Control-4	3.9	0.128	2.14	8.9×10^{-3}	0.41	0.21	0.30	0.15
Control-7	3.6	0.139	1.79	9.3×10^{-3}	0,43	0.23	0.35	0.18
Amended-1	6.3	0.591	<dl	<dl	0.08	0.10	<dl	0.07
Amended-4	5.8	0.340	<dl	4.0×10^{-2}	<dl	0.06	<dl	0.11
Amended-7	5.7	0.114	<dl	4.8×10^{-2}	<dl	0.32	<dl	<dl
				Crushed pyrite+smelting ashes				
Control-1	2.1	53.8	2.64×10^{3}	171	658	12.5×10^{3}	2.00	836
Control-4	1.2	111.6	3.19×10^{3}	131	832	23.2×10^{3}	3.10	1.01×10^{3}
Control-7	1.1	nd	151	14.5	92.6	2.44×10^{3}	2.28	62.9
Amended-1	5.1	13.4	844	0.144	117	34.8	0.40	404
Amended-4	2.6	24.0	1.85×10^{3}	2.86	224	2.43×10^{3}	0.57	321
Amended-7	2.2	nd	1.09×10^{3}	2.50	281	1.13×10^{3}	0.47	292

dl – detection limit; nd – not determined

The results show that the *gossan* is attaining a steady state as there are not noticeable changes in the measured parameters with time. On the other hand the crushed pyrite+smelting ashes are still reactive but its activity seems being decreasing with time. The limestone initially added disappeared after one month, dissolved by the continuous formation of sulfuric acid. The changes in pH are related with the amounts of sulfuric acid being generated by the system. The concentrations of aluminium in the leachate waters are very dependent on the pH as the dissolved amounts of this element are much higher in the amended media with low pH. The observed increase of dissolved aluminium in the amended soils has its origin in the used rockwool (from basaltic rocks). With exception of aluminium the used amendments seem to contribute to a decrease of the total elemental concentrations in the leachates in spite of the extreme conditions generated by the pyrite containing media.

The analysis of the data must consider the time evolution of a confined system subjected to continuous leaching by percolating raining water and the inner processes related with adsorption/desorption, complexation with organic matter, and crystallization that can occur in the time scale of the environmental processes.

Arsenic in natural aqueous systems. What a challenge!

MAGALHãES, Maria Clara (Universidade de Aveiro)

Arsenic is a chemical element that can be widely found in some particular environments as a result of natural geological processes or anthropic activity (sedimentary basins containing arsenic rich sediments; volcanic areas; mining areas; areas where arsenic containing biocides were intensively used; etc.), and it is poisoning human populations in some regions of the Earth. Arsenic ingestion may be voluntarily, as a result of traditional practices (for instance, arsenic wine in China) or the use of medicines, or involuntarily by drinking and/or eating naturally contaminated water and food. The toxicity of arsenic depends on its oxidation state, being the most commons –3, 0, +3 or +5; its species — inorganic species are considered more toxic then the organic ones; the physical state (arsane is a gas at 298 K and standard pressure); the solubility in water of the arsenic containing compounds; and the duration of exposure to arsenic containing media. Arsenic compounds have been used in paints and dyes, in biocides (algaecides, herbicides, insecticides, pesticides), in chemical warfare (agent blue), in wood preservatives, in medicine (organoarsenic compounds were discovered and used in the beginning of the XXth century for the cure of syphilis, cancer chemotherapy, etc.), and nowadays is widely used in electronics industry in LASER, light-emission diodes, semiconductors, and many other devices.

In a natural environment, in contact with a normal atmosphere, arsenate(V) are the most stable phases, but when the media become more reducing, as is the case of flooded soils, arsenic can be converted in arsenate(III) species, which are more mobile and considered more toxic than the arsenate(V) species. Arsenic contaminated water is the main source of arsenic intake in the body. In drinking water, the maximum contaminant level for arsenic was proposed by the World Health Organization (WHO) to be 0.010 mg As/L that has been followed in many countries. Normal natural waters contain, in general, concentrations of total arsenic lower than 0.010 mg As/L [1]. However, to decrease the arsenic concentrations in contaminated waters to levels lower than 0.010 mg As/L, in order to follow the WHO recommendations to drinking water, has been a big challenge. In spite of the huge efforts of several research groups, around the world, it has not been easy to find processes that originate drinking water with so low concentrations of total arsenic. Some organizations are already proposing a new maximum contaminant level for arsenic in drinking water of 0.005 mg As/L. Which statements support this proposal? Which will be the

impact in the human health? At present it is not clear that arsenic is not an essential element for human and other living beings.
The solid phases (rocks and minerals) play an important role in biogeochemical cycles of any chemical element. By dissolution their constituents are released to the aqueous solutions which can later be removed by the formation of new less soluble solid phases.
To understand the behaviour of arsenic containing compounds it is fundamental to have reliable thermodynamic constants for the acid ionization processes, species formation both in aquatic environments and solid phases, as well as other thermodynamic parameters. Arsenic compounds have not been deeply studied but information exists about the composition of many arsenic-containing minerals and description of their paragenetic sequences. However, the lack of thermodynamic parameters do not allow to model and infer their conditions of stability and their possible use as arsenic dispersion controllers. An overview of the present knowledge on arsenic compounds with environmental interest will be presented.[1] M. Williams, Arsenic in mine waters: an international study, Environ. Geol. 40 (2001) 267-278.

Thermodynamics of aqueous solutions of aliphatic ionenes with halide counterions

VLACHY, Vojko (University of Ljubljana) ; ČEBAšEK, Sašo (University of Ljubljana) ; LUKšIč, Miha (University of Ljubljana) ; POHAR, Ciril (University of Ljubljana)

Results for the enthalpy of dilution of aqueous solutions of 3,3−, 4,5−, 6,6−, and 6,9− ionenes with halide counterions were combined with the osmotic measurements to obtain the Gibbs free energy and entropy changes upon this process.
Enthalpies of dilution of aqueous solutions of aliphatic x,y−ionene fluorides and iodides, with x,y being equal to 3,3−, 4,5−, 6,6−, and 6,9−, were at 298 K measured in the concentration range from 0.1 mol kg−1 to 0.0016 mol kg−1. The results were combined with previously obtained data for ionene chlorides and bromides (1) to discuss the ion−specific effects in these solutions. The comparison with theoretical results, based on Manning's limiting law and cylindrical cell model founded on the solution of Poisson−Boltzmann's equation, is performed. These theories imply the enthalpy of dilution to be exothermic. Of all the solutions studied here, only those with fluoride ions as counterions agree with theoretical predictions. Solutions of 3,3−, 4,5−, and 6,6−ionene with bromide, chloride, and iodide counterions yield endothermic effect upon dilution. For the most hydrophobic 6,9− ionene, heat is released when adding water in the low concentration regime. Using the previously measured osmotic pressures for x,y−ionene bromides and chlorides (2), we calculated the Gibbs free energy and the entropy changes upon dilution. If the ionene halides of a given charge density are ordered upon the ΔH effect that they produce in solution (beginning with the exothermic and ending with the most endothermic) the Hofmeister series is obtained: F− > Cl− > Br− > I−. The non−Coulomb contributions to the Gibbs free energy, enthalpy, and entropy of dilution for solutions with bromide and chloride counterions were estimated (3). Results of the analysis indicate that the non−Coulomb contribution to TΔS varies

from being positive for 3,3− and 4,5−ionenes to negative for 6,6− and 6,9−ionenes. The results are consistent with recent measurements of enthalpies of mixing of x,y−ionenes with various sodium halide salts (4).

References:
(1) K. Arh, C. Pohar, Acta Chim. Slov. 2001, 48, 385. (2) K. Arh, C. Pohar, V. Vlachy, J. Phys. Chem. B 2002, 106, 9967. (3) S. Čebašek, M. Lukšič, C. Pohar, V. Vlachy, J. Chem. Eng. Data 2011, 56, 1282. (4) M. Bončina, M. Lukšič, M. Druchok, V. Vlachy, 2011, to be submitted.

The effect of solvent molecule and co-existing alkali cation on the luminescence of tris (oxalato) chromate(III) and tris(malonato)chromate(III) in the glassed mixed-solvent of water and ethanol at 77 K.

OTSUKA, Takuhiro (Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology) ; KAIZU, Youkoh (Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology)

Luminescence spectra, intensity and lifetime of the complex ions of tris(oxalato)chromate(III) ([Cr(ox)3]3-; ox2- = (COO-)2) and tris(malonato)chromate(III) ([Cr(mal)3]3--; mal2- = CH2(COO-)2) in the glassed mix- solvent of water and ethanol at 77K are very sensitive not only to the ratio of water and ethanol but also to the concentration of co-existing alkali cation.We will discuss the effect of the solvent molecule and alkali cation on the luminescence properties.

Introduction The luminescence spectra, intensity and lifetime of [Cr(ox)3]3- were studied in crystals of single complex salts (M3[Cr(ox)3]·nH2O; M+ = Li+, Na+, K+) 1) and double complex salts (M[Ru(bpy)3] [Cr(ox)3]·nH2O etc.) 2) at 77 K. The luminescence properties of the chromate(III) complexes are very sensitive to the solvent water molecule and co-existing alkali cation. In this study, we measured the luminescence spectra and lifetime of [Cr(ox)3]3- and [Cr(mal)3]3- in glassed mix-solvent of water and ethanol at 77K by changing the ratio of water and ethanol (v/v) and the concentration of co-existing alkali cations.

Results K3[Cr(ox)3] and K3[Cr(mal)3] emit strong phosphorescence in the mixed-solvent where the ratio of water/ethanol (v/v) is 50/50 ~ 70/30 at 77K. The luminescence maxima and lifetimes are 694nm and 1.0ms for K3[Cr(ox)3] and 688nm and 1.5ms for K3[Cr(mal)3]. In mixed-solvent of more than 80/20, the luminescence of K3[Cr(ox)3] is completely quenched. However, in K3[Cr(mal)3], new luminescence peak appears at 695nm and the lifetime is very short (5us). The luminescence of K3[Cr(ox)3] and K3[Cr(mal)3] is also affected by the concentration of co-existing alkali cation. Moreover, the luminescence and lifetime of Li3[Cr(ox)3] and Li3[Cr(mal)3] were also measured. We will discuss the effect of solvent molecule and co-existing alkali cation on the luminescence property

References: 1) T.Otsuka, et.al., Bull.Chem.Soc.Jpn., Vol.65, pp.3378, 1992. 2) T.Otsuka, et.al. Inog.Chem., No.38, pp.1340, 1999.; Inorg.Chem., No. 40, pp. 3406, 2001.

Dynamic properties of charged nanoparticles in solution from coarse-grained simulations

JARDAT, Marie (UPMC, France) ; DAHIREL, Vincent (UPMC, France) ; DUFRêCHE, Jean-françois (Université de Montpellier, France) ; TURQ, Pierre (UPMC, France)

I will present a multiscale strategy based on the Brownian dynamics simulation method, which leads to an approximate but realistic reproduction of the dynamics of charged nanoparticles in suspension. The coarse-graining procedure leads to a description where only the translational degrees of freedom of the nanoparticles are left, all the degrees of freedom related to the smallest solutes being averaged out. This very efficient simulation method allowed us to deduce from two different experimental methods (Pulsed field Gradient Nuclear Magnetic Resonance and Dynamic Light Scattering) the size and the charge of micelles in presence of added salt. This new simulation procedure is particularly useful when electrostatic interactions between small ions and nanoparticles have a strong impact on the transport properties of nanoparticles.

Computational Studies of Self-Assembly: From Surfactants and Janus Dendrimers to Ionic Liquids and More

KLEIN, Michael (Temple University)

2011 is The Year of Chemistry – However, the core science subjects: Chemistry, Physics, Mathematics, Biology are no longer adequate descriptors of what most scientists do! For example, modern chemistry explores interfaces – hard inorganic or organic (and/or nano) matter with soft materials – systems that will have a key role for 21st century applications – impacting energy and sustainability & more! Future technologies will need innovation in advanced materials. The pathway from discovery to applications demands chemists, physicist, and engineers work together also with researchers in industry. Computation will play an indispensible role in the path from discovery to application. The past decade has seen enormous progress in the broad application of computation to topical problems in science and engineering. By selected examples I will illustrate the current status of the field that employs computer simulation methodologies based on the principles of quantum mechanics and statistical mechanics to problems at the interface between chemistry and materials science. I will emphasize mostly softer materials, and the linking of their molecular design (chemistry) to boutique applications. The overarching theme is SELF-ASSEMBLY. The prospects for future applications in the biomedical arena will also be touched on, albeit briefly.

Vibrational spectral diffusion and molecular motion in supercritical water and aqueous solutions

CHANDRA, Amalendu (Indian Institute of Technology Kanpur)

A first principles theoretical study of vibrational spectral diffusion and molecular dynamics in supercritical water and aqueous solutions is presented through ab initio molecular dynamics and time series analysis. The time dependent changes of vibrational frequencies of OD stretch modes due to environmental fluctuations are calculated for pure water and aqueous ionic solutions under supercritical conditions. The frequency fluctuations are subsequently used to calculate spectral diffusion and frequency correlation functions to connect the dynamics of hydrogen bonds and dangling OD groups [1] to ultrafast vibrational spectroscopy [2]. Results for supercritical water and aqueous solutions are also compared with those under ambient conditions [3-5]. Results are also presented for simple chemical reactions such as proton transfer processes in supercritical water.

References

1. B.S. Mallik and A. Chandra, J. Phys. Chem. A 112, 13518 (2008); Chem. Phys. (2011), in press.
2. D. Schwarzer, J.Lindner and P. Voehringer, J. Chem. Phys. 123, 161105 (2005); J. Phys. Chem. A 110, 2858 (2006).
3. B.S. Mallik, A. Semparithi and A. Chandra, J. Phys. Chem. A 112, 5104 (2008); J. Chem. Phys. 129, 194512 (2008).
4. C.J. Fecko, J.J. Loparo, S.T. Roberts and A. Tokmakoff, J. Chem. Phys. 122, 054506 (2005); S. Park and M.D. Fayer, Proc. Natl. Acad. Sci.104, 16731 (2007); M.F. Kropman and H.J. Bakker, Science, 291, 2118 (2001).
5. R. Rey, K.B. Moeller and J.T. Hynes, J. Phys. Chem. A 106, 11993 (2002); C.P. Lawrence and J.L. Skinner, J. Chem. Phys. 118, 264 (2003); B. Nigro, S. Re, D. Laage, R. Rey and J.T. Hynes, J. Phys. Chem. A 110, 11237 (2006).

Thermochemistry related to the liquid-liquid extraction of cations

CHARBONNEL, Marie-christine (CEA)

In the nuclear field and specifically for the treatment of high-level liquid waste, different actinide recycling options are considered to reduce the volume and the toxicity of ultimate waste. Different strategies have been tested to separate minor actinides, alone or with other actinides. For each way, specific molecules were designed and the relevant ligands were selected with several criteria, among them of course the performance in terms of chemical affinity and selectivity towards the actinide target. In order to gain a deeper understanding of distribution of actinides along the liquid-liquid process, molecular studies have been undertaken with both structural and thermodynamic approaches.

The presentation will focus on the thermodynamic properties (free energy $*G°$, enthalpy $*H°$ and entropy $*S°$) related to the extraction of actinides and lanthanides with a strong link with speciation studies. Extraction enthalpies and entropies can be obtained from the temperature-dependence of Kext (called Van t'Hoff method) or from microcalorimetry. The main interest of titration calorimetry is that studies can provide molecular information on the different interactions (between ligand and diluent, ligand and cation, ligand and ligand) and therefore allow the identification fo the driving forces of the extraction. However the representative chemical process conditions for actinide extraction are not ideal from the thermodynamic point of view. To obtain valuable results, the first point is the knowledge of the speciation to be able to describe the systems with the appropriate equilibriums. Then dedicated studies are necessary to eliminate heat signals due to side reactions (actinide activity, high ionic forces due to important salts concentration, biphasic systems). Some exhaustive studies performed with this 'multitechnical' approach will be presented.

Friedman's Excess Free Energy and the McMillan-Mayer Theory of Solutions

GóMEZ-ESTéVEZ, Juan Luis (Universitat de Barcelona)

In his version of the theory of multicomponent systems, Friedman used(1,2), the analogy which exists between the virial expansion for a real gas and the corresponding expansion for the osmotic pressure obtained from the McMillan-Mayer (MM) theory of solutions(3). For the calculation of the thermodynamic properties of the solution, a definition for the "excess free energy" that remenbers the ancient idea for the "osmotic work" was proposed by him. However, the precise meaning to be attached to his free energy is, apart from other reasons(4), not well defined because in osmotic equilibrium the solution is not a closed system and for a given process the total amount of solvent varies. In this work, a thermodynamical analysis is first presented in order to obtain and exact definition for Friedman's excess free energy. Secondly, the precise relationship with the MM theory which was formulated originally in the grand canonical ensemble(3), is given. This las step is done by translating the original MM theory to a semigrand canonical ensemble for the solute(s) particles without the explicit presence of the solvent but interacting among themselves through a potential of mean force at infinite dilution.

1.-Friedman,H.L.,"Thermodynamic Excess Functions for Electrolyte Solutions";J.Chem.Phys.,32(1960),1351-1362. 2.-Friedman,H.L.,"Density Expansions of Correlation Functions for Equilibrium Systems";J.Chem.Phys.,34(1961),73-78.
3.-McMillan,W.G.,Mayer,J.E.,"The Statistical Thermodynamics of Multicomponent Systems";J.Chem.Phys.,13(1945),276-305. 4.-Friedman,H.L.,Dale,W.D.T.,"Electrolyte Solutions at Equilibrium" in Statistical Mechanics.Part A: Equilibrium Techniques.B.J. Berne(Editor).Plenum Press,New York and London, 1997.

Fluids in porous media :Theory and computer simulations.

HOLOVKO, Myroslav (Institute for Condensed Matter Physics) ; PATSAHAN, Taras (Institute for Condensed Matter Physics) ; SCHOTOLOKHA, Volodymyr (Institute for Condensed Matter Physics) ; DONG, Wei (Ecole Normale de Lyon)

In this report we present some recent results of our theoretical investigations of thermodynamic properties of fluids confined in random porous media. We consider three types of porous media depicted by the corresponding models known in the literature as hard sphere, overlapping hard sphere and hard sponge matrices. In the beginning, we discuss the exact results for an ideal gas in such porous media [1]. Then, we present the extension of the scaled particle theory that allows us to obtain analytical expressions of the both chemical potential and equation of state for a hard sphere fluid confined in the random porous media. The developed approach is based on a combination of the exact treatment of a point scaled particle in the system of a hard sphere fluid confined in matrix and the thermodynamic consideration of a finite-size scaled particle. It is observed that the theory leads to highly accurate expressions for the fluid chemical potential over the whole density range with errors comparable to the computer simulation results [2, 3]. We also propose the generalization of the scaled particle theory to the case of a hard convex-body fluid confined in random hard convex-body matrices. The results obtained in our study can be used as reference systems for the description of more realistic models of a fluid. As an example, we consider the extension of the van der Waals equation of state for a simple fluid in random matrices. We also discuss the combination of the scaled particle theory with the integral equation theory applied to ionic, associative and some other fluids confined in the random porous media. The possibilities of mapping of the thermodynamic properties of fluids in random porous media of different types are presented in the end. As is shown, the isotherms of fluid in the different matrices tend to be equivalent if porosities and specific surface pore areas of these matrices are identical.

[1] Dong W. Condens. Matter Phys. 10 (2007) 509. [2] Holovko M., Dong W., J. Phys. Chem. B 133 (2009) 6360. [3] Patsahan T., Holovko M., Dong W., J. Chem. Phys. 134 (2011) 074503.

Cryo-brines - a new field for solution chemistry?

VOIGT, Wolfgang (TU Bergakademie Freiberg) ; HENNINGS, Erik (TU Bergakademie Freiberg)

Recent findings from Phoenix Lander Mars mission strongly suggest the presence of liquid aqueous salt solutions on Mars surface, despite temperatures as low as 190 K as was first postulated by N. Renno [1]. Existence of aqueous solutions concerns the questions of habitability of life [2].

From remote sensing investigations it is known, that on the Martian surface large amounts of salts like halides or sulfates of alkali or alkaline earth metals are deposited. In-situ analysis at Phoenix Lander provided even evidence for the presence of perchlorates in appreciable amounts. These and other facts raised the question which cation-anion combinations can form liquid aqueous solutions at very low temperatures and low pressures of about 600 Pa. Möhlmann, who created the term "cryo-brines" listed some examples of electrolyte solutions, which can meet these requirements on Mars at least temporarily [3]. Stimulated from the on-going discussion and the above mentioned authors we made an extensive literature search for phase equilibria and physico-chemical properties of water-salt systems with low eutectic temperatures. Freezing curves of 195 binary systems and the few available data for ternary systems have been evaluated in respect to the freezing point depression and trends in the activity coefficients of water along the ice curves. As a result it has to be stated that cryo-brines have not been studied systematically. Exceptions are the few systems (HNO3, H2SO4, (NH4)2SO4) with interest in the tropospheric research. Beside freezing curves no further thermodynamic data are available for $T < 250$ K. Often the composition of the co-existing hydrate phase at the assumed eutectic is not clear or unknown. Furthermore, on the basis of the present theory of electrolyte solutions it is not possible to predict tendencies in ion association or ion hydration when lowering the temperature to such an extent. Even traditional terms in solution chemistry like structure-breaking, structure- forming or Debye-Hückel slope loose their meaning, because liquid water as a reference does not exist below 240 K. New experimental investigations will be necessary to get inside into structure - property relations of cryo-brines. On the other hand cryo-brines open the possibility to study species and systems not stable at room temperature conditions as for example hydrated cations of higher valency like Sn4+.

[1] Renno, N.O., B.J. Bos, D. Catling, B.C. Clark, L. Drube, D. Fisher, W. Goetz, S.F. Hviid, H. Keller, J.F. Kok, S.P. Kounaves, K. Leer, M. Lemmon, M. Bo Madsen, W. Markiewicz, J. Marshall, C. McKay, M. Mehta, M. Smith, M.P. Zorzano, P.H. Smith, C. Stoker, S.M.M. Young. Possible physical and Thermodynamical Evidence for Liquid Water on the Phoenix Landing Site. Geophys. Res., 114(2009), E00E03

[2] Davila, S.A.F., Duport, L.G., Melchiorri, R. Jänchen, J., Valea, S., de los Rios, A., Fairén, A.G., Möhlmann, D. , McKay, C.P., Ascaso, C., Wierzchos, J., Hygroscopic Salts and the Potential for Life on Mars, Astrobiology 10(2010)6, 617-628

[3] Möhlmann, D.T.F., Latitudinal distribution of temporary liquid cryo-brines on Mars, Icarus 214 (2011) 236–239

Aqueous solutions of hydrophilic and hydrophobic amino acids

TEIXEIRA, José (Laboratoire Léon Brillouin (CEA/CNRS)) ; RUSSO, Daniela (CNR-IOM c/o Institut Laue Langevin, 6 rue J. Horowitz BP156, F 38042 Grenoble)

We investigate the dynamics of aqueous solutions of peptides containing hydrophobic side-chains. We compare the internal dynamics of the amino acid N-acetyl-leucine- methylamide, containing a hydrophobic side chain with N-acetyl-glycine-methylamide, which comprises only the same polar backbone.

We follow the dynamics of hydration water from hydrated powders to concentrated solutions as a function of temperature. The study of rotational and diffusion motions by quasi-elastic neutron scattering shows a dynamical transition at about 250 K for long side chain peptides while, in

absence of side chains, there is no dynamical transition. We emphasize that the side chain length has a role on the onset of the dynamical transition.
The analysis of the vibrational density of states demonstrates that the density of hydration water at hydrophilic interfaces is similar to that of dense amorphous ice while, at the vicinity of extended hydrophobic regions, the density is that of low density amorphous ice. The high frequency modes show a blue shift of the libration mode as compared to the room temperature data.

Standard State Thermodynamic Properties for Ionization of Water up to 573.15 K

DJAMALI, Essmaiil (San Diego State University)

In the literature, there is an apparent disagreement in the values of the standard state thermodynamic properties for ionization of water calculated from potentiometric [1] and calorimetric measurements [2] at temperatures T > 473 K. Conclusions have been drawn based on incomplete sets of data available at the time about this apparent disagreement [3, 4]. Using ionic additivity, values for the changes in the standard state Gibbs free energy, enthalpy, entropy, heat capacity, and molar volume for ionization of water, at steam saturated pressure up to the temperature of 573.15 K, are calculated from the recently available corresponding values for the standard state partial molar properties of HCl(aq) [5], NaCl(aq) [6], and NaOH(aq) [4, 7]. Comparison of the present study with the literature data indicate that in fact there are no disagreements between the above mentioned standard state thermodynamic properties for ionization of water calculated from potentiometric and calorimetric measurements. The apparent disagreement is, however, the result of the model chosen to represent the potentiometric data.
References:

1. F.H. Sweeton, R.E. Mesmer, C.F. Baes, Jr., J. Solution Chem. 3 (1974) 191–214. 2. X. Chen, J.L. Oscarson, S.E. Gillespie, H. Cao, R.M. Izatt, J. Solution Chem. 23 (1994) 747–768. 3. A.V. Sharygin, R.H. Wood J. Chem. Thermodyn., 29 (1997)125–148.
4. S. Schrodle, E. Konigsberger, P.M. May, G. Hefter, Geochim. Cosmochim. Acta. 72 (2008) 3124–3138. 5. E. Djamali, J.W. Cobble, J. Phys. Chem. B 113 (2009) 10792–10799. 6. E. Djamali, J.W. Cobble, J. Phys. Chem. B 113 (2009) 5200–5207.
7. J.M. Simonson, R.E. Mesmer, P.S.Z. Rogers, J. Chem. Thermodyn. 21 (1989) 561–584.

Chemical template synthesis of polypyrrole nanowire arrays and their hydrogen gas sensing properties

OMIDVAR, Hamid (assistant de prof) Mlle. HASSANZADEH, Nafiseh (Thésard)

Gas sensors based on conducting polymers such as polypyrrole, possess advantages in comparison to metal-oxide gas sensors due to their capability to detect gases at room temperature. Nanowires are attractive for gas sensing applications owing to their high surface to volume ratio, as gas sensors response often rely on gas molecules- surface interactions. In the current research, high density and long polypyrrole nanowire arrays with aspect ratio of about 300, were synthesized inside the nanochannels of alumina membrane through chemical polymerization using a two compartment cell. The obtained nanostructures were characterized by SEM, FTIR and BET techniques. The effects of polymerization time and temperature and also the molar ratio of oxidizing agent ($FeCl3$) : monomer (pyrrole) on the alumina membrane pores filling were investigated. Synthesizing at room temperature for 3 hours was determined as the proper fabricating condition. The maximum surface area of the nanowire arrays was 172.90 at $FeCl3$:Py molar ratio of 1:1 with each reagent concentration of 0.2 M. The conductometric hydrogen gas sensing of polypyrrole nanowire arrays was investigated at room temperature. The results show that the electrical resistance of the sensor reduced upon exposure to hydrogen gas. The maximum sensitivity was 1.03% to 12000 ppm $H2$.

Ultrasoft primitive model of polyelectrolytes in solution

COSLOVICH, Daniele (Université Montpellier 2) ; HANSEN, Jean-pierre (University of Cambridge) ; KAHL, Gerhard (Tecnische Universitat Wien)

We will review recent results on primitive models of oppositely charged polyions and present a new, ultrasoft core model of interpenetrating polycations and polyanions with continuous Gaussian charge distributions. The model aims at investigating the aggregation process ("complex coacervation") of ultrasoft polyelectrolytes in dilute and semi-dilute solutions, in the absence [1,2] and presence [3] of added salt. In the salt-free case, the effective interaction between the polyions is given by a bounded potential at short distances and a long-range Coulomb interaction. By means of numerical simulations, we show that the topology of the phase diagram of the symmetric version of the model (the ``ultrasoft restricted primitive model") differ from that of the widely studied ``restricted primitive model" (RPM), where ions have hard cores. At sufficiently low temperatures and densities, oppositely charged polyions form weakly interacting, polarizable neutral pairs, leading to a sharp conductor-insulator transition. The conductor-insulator transition line terminates near the top of a first order coexistence curve separating a high-density liquid phase from a low-density vapor phase. The simulation data thus hint at a tricritical behavior, reminiscent of that observed in the two-dimensional Coulomb Gas, which contrasts with the Ising criticality of its three-dimensional counterpart, the RPM. The effect of salt addition on the physical properties of the model and the possible aggregation patterns in the asymmetric version of the model will be briefly discussed.

[1] D. Coslovich, J.-P. Hansen, and G. Kahl, Soft Matter 7, 1690 (2011) [2] D. Coslovich, J.-P. Hansen, and G. Kahl, J. Chem. Phys. 134, 244514 (2011) [3] D. Coslovich, J.-P. Hansen, and G. Kahl, submitted to Mol. Phys. (2011)

Speciation of uranyl nitrate in organic phases containing monoamide extractant

FERRU, Geoffroy (CEA Marcoule) ; BERTHON, Laurence (CEA) ; SOREL, Christian (CEA) ; SIMONIN, Jean-pierre (CNRS)

In order to aid the understanding of the phenomena occuring during actinides extraction in hydrometallurgical processes of spent nuclear fuel, we have focused our study on the extraction of uranyl nitrate by a monoamide (N,N-diethylhexylisobutyramide, DEHiBA), diluted in an aliphatic solvent. An effort has been made to investigate the speciation of such organic phases at the molecular and supramolecular scale in relation to the concentration of extractant, uranyl nitrate and co-extracted water. This experimental part was carried out together with the thermodynamic modeling of the solvent extraction equilibriums. Molecular complexes were characterized by Infra Red spectroscopy, Time-Resolved Laser Induced Fluorescence Spectroscopy (TR-LIFS) and Electro-Spray Ionization Mass Spectrometry (ESI-MS). These techniques provide information about the interaction between extractant and uranyl nitrate, and the number and stoichiometry of the organic species. On the basis of this information, chemical equilibriums have been proposed to model the extraction of uranyl nitrate by DEHiBA. The organization (or aggregation?) of the organic phase has also been studied by NMR spectroscopy and Small Angle X ray Scattering (SAXS).

Adsorption and Dynamics of Water and Ions in Nanopores

COASNE, Benoit (Institut Charles Gerhardt Montpellier - CNRS) ; SIBOULET, Bertrand (Institut de Chimie Séparative de Marcoule) ; DUFRECHE, Jean-francois (Institut de Chimie Séparative de Marcoule) ; TURQ, Pierre (Institut de Chimie Séparative de Marcoule) ; BONNAUD, Patrick (Massachusetts Institute of Technology) ; PELLENQ, Roland (Massachusetts Institute of Technology) ; CAZADE, Pierre-andre (Institut Charles Gerhardt Montpellier)

Water and ions confined in pores or in contact with a surface are systems commonly encountered in Geology, Biology, Physics, and Chemistry. From a practical point of view, these systems are of particular relevance to applications ranging from nanofiltration to catalysis, phase separation, and materials for construction (concrete). As a result, important research efforts have been devoted to understand the effect of confinement and surface forces on the thermodynamics and dynamics of water and ions. Nevertheless, while significant insights into the structure and

dynamics of water have been gained, the role of the ions on the overall behavior of the nanoconfined system still needs to be addressed.

In this presentation, we will report recent results obtained for water and ions confined in nanopores. By considering both carbon1 and silica2,3 nanopores of various sizes, we will investigate the effect of surface chemistry and pore size on the thermodynamics (adsorption), structure, and dynamics of confined water and ions. In the specific case of silica, we will report both ideal models of silica surfaces obtained by cutting surfaces from crystalline materials2 and a realistic model obtained using simulated annealing simulations3. We will show how the hydrophilicity of the surface can be tuned by varying the amount of silanol groups at the pore surface. In a first step, we will investigate the adsorption of water and ions in the different nanopores using Grand Canonical Monte Carlo (GCMC) simulations. The structure and orientation of confined water and ions will be determined by means of density profiles, hydration/solvation numbers, and suitable order parameters. In particular, we will discuss the effect of surface forces and confinement on the orientation of water with respect to the silica surface and its tetrahedral organization. In a second step, starting from well equilibrated configurations obtained from GCMC simulations, we will determine the self diffusivity and transport of water and ions confined within the nanopores. We will discuss our results in the light of the classical model of the electrical double layer for electrolyte solutions in contact with a solid surface. Special attention will be also paid to the effect of confinement and surface interactions on transport properties related to electrokinetic phenomena such as electro-osmosis.

1. P. A. Cazade, J. Dweik, B. Coasne, F. Henn, J. Palmeri, Structure and dynamics of electrolyte solutions confined in nanopores, J. Phys. Chem. C 114, 12245 (2010). 2. P. Bonnaud, B. Coasne, R. J. M. Pellenq, Molecular simulation of water confined in nanoporous silica, J. Phys. Condens. Matter, 22, 284110 (2010).
3. B. Siboulet, B. Coasne, J. F. Dufreche, P. Turq, Hydrophobic to hydrophilic transition in a realistic model of amorphous silica surfaces, J. Phys. Chem. B 115, 7881 (2011).

Transport and thermodynamic properties of complex mixed electrolytes : Modeling within the Mean Spherical Approximation

BERNARD, Olivier (UPMC) ROGER, Gaelle (ONERA) ; AUPIAIS, Jean (CEA) ; TURQ, Pierre (UPMC)

In many studies of electrolyte, solutions can be concentrated, by their origin or in order to improve the measurements . For example, in order to improve the resolution of electrophoresis peaks, the measurements are often made in the presence of a concentrated solution of a supporting electrolyte. The exact position of the electrophoresis peaks can be strongly affected by the presence of this supporting electrolyte. Theoretical models currenty used in this field (Debye Hückel or extended Debye Onsager Bjerrum models) are limited to the 0.01M to 0.1M range, at least for the non ideality in transport, even if empirical models for the non ideality in thermodynamics (activity coefficients) can be used for the static part. However progress in the transport theories, have been made in the last decade, for self and mutual diffusion, individual or

global conductivity . Those models allow to describe quantitavely the evolution of those transport coefficients for concentrations of the order of 1 to 2 M for small electrolyte mixtures and are also convenient to describe highly charged species in solutions such as micelles formed in ionic surfactants solutions .
On the other hand, the characterization of highly charged ions requires to take into account the formation of the different physico-chemical complexes between the different ions in solution and in the surrounding such as hydroxyde, carbonate, sulphate. For higher concentrations, the consideration of departures from ideality since the time of Debye or Pitzer allow for the description of osmotic and activity coefficients in a satisfying manner for very high concentrations within the Mean Spherical Approximation (MSA).
It is then possible to consider the modelisation of complex electrolyte solutions with both transport and equilibrium non idealities, as well as speciation phenomena (complex formation). As an example we describe also the migration of trace elements in supporting electrolyte with buffercouple (to fix pH), speciation and non ideality treated by MSA.

Mobility of charged colloids by electroacoustics

DUBOIS, Emmanuelle (UPMC PECSA) ; PUSSET, Raphaël (UPMC PECSA) ; BERNARD, Olivier (UPMC PECSA) ; CHEVALET, Jean (jean.chevalet@upmc.fr) ; DURAND-VIDAL, Serge (UPMC PECSA) ; MéRIGUET, Guillaume (UPMC PECSA)

The mobility of charged colloids is a key parameter of such systems, as it depends on their electric charge, and thus controls their properties and their colloidal stability, which is crucial in their uses and applications. Often measured by laser velocimetry, the electrophoretic mobility is usually translated into zeta potential. This technique is limited to dilute systems due to the optic detection. The mobility can however also be obtained by electroacoustics : the principle is to analyze the electric answer of the colloidal suspension submitted to an acoustic wave, or the inverse process, i.e. the acoustic wave induced by an electric field applied to the colloidal suspension [1]. Although this technique is seldom used, it is the only one adapted to concentrated and dark systems, which are numerous (milk, paint, cement). They can be studied without dilution thus without any modification. After a presentation of the technique, we will show some examples of results of the charged properties of small colloidal suspensions, especially on nanometric objects. Cross comparison with other techniques is presented for representative systems.
[1] A.V. Delgado et al, Pure Appl.Chem., Vol.77, No.10, pp.1753–1805, 2005.

Exploring Life Phenomena with a Statistical Mechanics of Molecular Solution

HIRATA, Fumio (Institute for Molecular Science)

It is a common understanding that the molecular recognition is an essential elementary process for protein to function. The molecular recognition is a thermodynamic process which is characterized by the free energy difference between two states of a host-guest system, bound and unbound. On the other hand, the time to reach the thermodynamic equilibrium depends on the free energy barrier mainly associated with the conformational fluctuation of protein. Therefore, the molecular recognition is a thermodynamic process conjugated with the conformational fluctuation of protein.

We have been developing a new theory for the molecular recognition by protein based on the statistical mechanics of liquids, or the 3D-RISM/RISM theory. The theory has demonstrated its amazing capability of "predicting" the process from the frist principle. [1] However, what we have investigated so far is an entirely equilibrium process both in protein conformation and solvation. Recently, we have started to incorporate the conformational fluctuation of protein into the molecular recognition process in two ways. The first of those is a "static" one in which we just shake the protein conformation to find the local minimum of the free energy surface by the combined 3D-RISM/RISM with conformational sampling algorithms, and to see if one can find the distribution of a guest molecule in the recognition site. One example of such studies will be presented in the talk. [2] The other method is to take the "dynamic" fluctuation of protein conformation into account. The process can be described by hybridized 3D-RISM/RISM with the generalized Langevin dynamics theories. The methodology is currently under construction, and some prospective view of the theory will be presented in the lecture.

REFERENCES [1] N. Yoshida, et. al., J. Phys. Chem. B(Feature Article), 113, 873 (2009). [2] Y. Kiyota, et. al., J. Am. Chem. Soc. (Communications), 131, 3852 (2009). [3] B.S. Kim, et. al., Cond. Matter Phys., 11, 179 (2008).

How well-behaved are electrolyte mixtures at high temperatures ?

HEFTER, Glenn (Murdoch University Western Australia)

Concentrated mixtures of electrolyte solutions are of great importance in the environment, for example in seawater and salt lakes, but also in many industrial processes. In economic terms the most significant of the latter is undoubtedly the well-known Bayer process, used for the extraction and purification of alumina from bauxite ores. Bayer process solutions are complex mixtures containing about ten major electrolyte components (and of course many minor components) with total ionic strengths that range from approximately zero to 6 mol/L. Reliable prediction of the physicochemical properties of such solutions is essential for process control and optimization. Unfortunately, it is not at present possible to describe accurately the properties even of individual (binary) electrolyte solutions from first principles, ie, without resort to empirical parameters, as used for example in the popular Pitzer models. Property description for mixtures of electrolytes becomes unmanageable when using such models because of the number of parameters that require optimisation. On the other hand, mixtures of electrolytes at ambient temperatures often show remarkably simple behaviour, expressed for example by Young's rule. Since many industrial processes operate at high temperatures, it is important to know whether or not this simple behaviour is retained. This talk will present recently measured data for the densities (molar volumes) and heat capacities of a range of electrolyte mixtures at temperatures up to 300°C, which address the question of how well-behaved are electrolyte mixtures at high temperatures.

Phase equilibria of binary and ternary systems containing ILs

ROONEY, David (Queen's University Belfast) ; HARDACRE, Chris (Queen's University Belfast) ; AB MANAN, Norfaizah (PETRONAS Research Sdn. Bhd.)

Recent interest in the measurement of multi-phase equilibria in ionic liquids has led to a rapid increase in available data. Using this information several attempts have been made to predict and estimate the activity coefficients needed for vapour-liquid, or liquid-liquid equilibria at different temperatures and pressures. These are generally categorised into four main families: Equation of State; Molecular Simulation, Group Contribution and Correlation Models (GCM). We have recently explore and evaluate the extent to which COSMOthermX may be used to predict the solubility of different gases in a range of ILs, and have shown that this tool can be used to estimate solubilities and predict correct trends in most cases. What is clear from this work is that the structure and environment are important factors in developing a suitable predictive model.
Using the understanding gained from the gas solubulity data this talk will further discuss the binary and ternary phase behaviour of ionic liquids for extracting cyclohexanecarboxylic acid (CCA) from a dodecane stream. This particular system was chosen as a model for the extraction of acids representative of naphthenic acids found in many crude oils. In order to develop an effective ternary liquid-liquid extraction system the preliminary selection of ionic liquids was based on the extent of CCA miscibility and the dodecane immiscibility with selected ILs. A wide range of ionic liquids based on different cations, anions, cation alkyl-chain length, as well as the effect of temperature on the overall fluid phase behaviour is reported. As expected tt was observed that factors such as variation of cation group, anion effect, alkyl-chain length, and temperature all impact the extraction to various degrees. The largest effects were found to be the lipophilicity of the ionic liquid cation and the co-ordination ability of the anion. While CCA capacity increased with lipophilicity of the cation, so too did the dodecane. Highly coordinating anions such as trifluoroacetate and triflate demonstrated that highly efficient extraction could be obtained producing favourable tie-lines in the ternary phase diagram. Overall, this study demonstrates that ionic liquids can selectively extract acids from hydrocarbon streams and thus offer possible treatment solutions for problems associated with the processing of high acid crude oils.

Some apsects of organic Chemistry in super heated water

GOETTMANN, Frédéric (CEA/DEN/ICSM)

At 200°C the chemical and physical properties of water are totally different from what we are used to: - the self dissociation constant of water reaches a maximum, with the proton concentration being three orders of magnitude higher than usual- the dielectric constant of water is already very low, making it a good organic solvent These considerations prompted us to investigate how super-heated water can be used as a solvent to perform organic synthesis and ion separation in a new greener way.

Cationic liposomes as gene delivery vehicles: the structure and binding capacity

UHRIKOVA, Daniela (Faculty of Pharmacy Comenius University) ; PULLMANNOVA, Petra (Faculty of Pharmacy Comenius University) ; HUBCIK, Lukas (Faculty of Pharmacy Comenius University) ; DEVINSKY, Ferdinand (Faculty of Pharmacy Comenius University) ; FUNARI, Sergio S. (Hasylab at DESY) ; BALGAVY, Pavol (Faculty of Pharmacy Comenius University)

The structure and polymorphic behaviour of complexes prepared by DNA interaction with cationic liposomes were studied by synchrotron small angle X-ray diffraction. Complexes are used as DNA delivery vectors. To best of our knowledge, the observed phase transition from cubic to condensed lamellar phase induced by pH has not been reported yet in the field of gene delivery vectors.

The interaction of DNA polyanion with a dispersion of cationic liposomes result in a formation of colloid particles of regular inner microstructure. They attract attention as a delivery vectors for genetic material. Despite the fact that cationic liposomes have been used for transfection, and commercial lipid formulations are available, their efficiency needs to be improved. Relationship between transfection efficiency, physico-chemical properties, their microstructure and polymorphic behaviour is still under discussion.

We will discuss structural diversity and binding capacity for DNA of two groups of complexes prepared from neutral phospholipids with positive charges created either by gemini surfactants (CnGS) or pH responsive N-alkyl-N,N-dimethylamine-N-oxides (CnNO). The binding capacity of complexes for DNA is in the range 30-95 % depending on the system and external conditions, as we derived from spectrophotometry. A small angle synchrotron X-ray diffraction (SAXD) was used to examine the microstructure of formed complexes. In addition to condensed lamellar (Lac) and inverted hexagonal (HIIc) phase, we identified the presence of cubic phases Q (Pn3m and Im3m space groups) in complexes prepared with CnNO. The surface charge density of cationic liposomes and the length of spacer of CnGS are a key parameters modulating Lac - HIIc phase transition observed in complexes with gemini surfactants. The second group, complexes with CnNO, have shown Q - Lac phase transition as a function of pH. Structural parameters of Lac phase, and the DNA-DNA distance are pH dependent. In this way, complexes prepared with CnNO represent pH responsive DNA nanocarriers. In the field of pharmacy, bicountinuos cubic phases attract attention as promising group of carriers for a large spectrum of drugs, genetic material (DNA, siRNA), small proteins or peptides including.

Cellular Automata Approach to Corrosion and Passivation Phenomena

STAFIEJ, Janusz (Institute of Physical Chemistry) ; DI CAPRIO, Dung (UMR7575 CNRS, LECIME l'ENSCP) ; BARTOSIK, Łukasz (Institute of Physical Chemistry)

The cellular automata based simulations on corrosion and passivation processes are reviewed. We discuss our results showing a variety of crossover phenomena involved in these processes. First we observe the crossover from slower to faster corrosion accompanied by anodic and cathodic zone separation. Then a crossover from the reaction controlled to diffusion controlled regime in the passive layer growth.

Finally we show crossover from the active to passive electrode state when changing polarization accompanied by morphological changes of the passive layer.

In this talk we review our work on corrosion and passivation done in collaboration of our laboratories over the past 5 years. We consider three topics of this work. The first topic is the appearance of anodic and cathodic zones on the corroding surface due to coupling of the corrosion process of a metal surface in an aggressive solution with the solution chemistry. The well known phenomenology of corrosion is that anodic metal dissolution at a depassivated site of the surface leads to acidification of the neighboring solution and enrichment in noxious anions that prevent repassivation and promote a further dissolution. In contrast cathodic reactions that occurs also on passivated surface lead most often to a basification of the neighbouring solution which is more beneficial in general for the passive layer. If we code this phenomenology in a form of a cellular automata model and perform simulations in 2D we observe a patchwork of zones of either cathodic and anodic character that arises spontaneously whenever the size of the simulated system is larger than the characteristic size. We find this size by a simple scaling argument. The model accounts for the well known paradoxes of corrosion – the faster homogenization of the solution by diffusion, convection or stirring the slower corrosion [1].

The second topic relates to a crossover phenomenon that may take place in the growth of passive layers. In our model the passive layer growth takes place by a redistribution of matter within the layer via a diffusion process. Then the layer growth kinetics and morphology display two time regimes. Initially for the thin layer the growth is controlled by the reaction rate with which the layer material is produced. In this regime the growth is simply proportional to time with a constant rate. Then it crosses over to the regime where the diffusion control imposes the growth proportional to the square root of time with the growth rate decaying as the inverse of the square root of time. The scaling relations for this crossover transition are found and discussed [2,3]. This model is rather of theoretical and illustrative interest rather than a real world description. The main shortcoming is that it never reaches a stationary state allowing for an indefinite growth of an infinitely thick layer. It does not account for the extremely low but finite solubility of the layer material.

The third topic deals with models that remove this shortcoming by including a process due to which the forming layer can lose its material. Then we can reach the stationary state and look at its properties as a function of the surface reactivity. For the same metal material it is set by the electric potential. We reproduce qualitatively the form of the potential current curve. In addition to this we obtain different morphological regimes for various models. At present we are looking for a model that would reproduce self organization of nanopores in passive layers. We show some successful first results [4,5].

Acknowledgements The support of the Polish Ministry of Science and Higher Education grant No NN 204 139038 is gratefully acknowledged. The work of Łukasz Bartosik was realized within the International PhD Projects Programme of the Foundation for Polish Science, cofinanced from European Regional Development Fund within Innovative Economy Operational Programme "Grants for innovation"

References. 1. Reis FDAA, Stafiej J, Badiali JP, JOURNAL OF PHYSICAL CHEMISTRY B 110 (35): 17554-17562, 2006 2. Reis FDAA, Stafiej J, JOURNAL OF PHYSICS-CONDENSED MATTER 19 (6): art. no. 065125, 2007 3. Reis FDAA, Stafiej J, PHYSICAL REVIEW E 76 (1): art. no. 011512, 2007 4. di Caprio D, Stafiej J, ELECTROCHIMICA ACTA 56 (11): 3963-3968, 2010 5. di Caprio D, Stafiej J ELECTROCHIMICA ACTA 55 (12): 3884-3890 2011

Dynamics and reactivity in confined media : From micropores to macropores

RENAULT, Jean Philippe (CEA/IRAMIS et CNRS UMR 3299 SIS2M, Laboratoire de Radiolyse) ; MUSAT, Raluca (CEA/IRAMIS et CNRS UMR 3299 SIS2M, Laboratoire de Radiolyse) ; LE CAER, Sophie (CEA/IRAMIS et CNRS UMR 3299 SIS2M, Laboratoire de Radiolyse) ; POMMERET, Stanislas (CEA/IRAMIS et CNRS UMR 3299 SIS2M, Laboratoire de Radiolyse)

As technology progresses to the nano-scale, the question of how chemical reactions are perturbed by the size of the environment needs further consideration. Radiolysis of liquids is promising tool to investigate chemical reactivity in complex environments and especially in confinement. As ionising radiations induce reactions throughout the entire sample, whatever its complexity, information on the chemical reactivity at the microscopic scale can be obtained from macroscopic analytical strategies. I will describe how confinement affects the fate of radiolytically produced radicals within water filled micro, meso and macropores compared to homogeneous solutions.[1-3]

These results will be put in line with the current understanding of the effect of confinement on the dynamics of confined molecules. In this respect, I will present our use of static and ultrafast infrared spectroscopy to probe the hydrogen bond network properties and thus investigated the dynamics of confined water. [4]

References

[1] S. Foley, P. Rotureau, S. Pin, G. Baldacchino, J. P. Renault and J. C. Mialocq. Angewandte Chem.-Int. Ed. 44 110 (2005] [2] R. Musat, G. Vigneron, D. Garzella, S. LeCaër, J.F. Hergott, J.P. Renault, S. Pommeret, (2010) Chem. Commun., 46, 2394 (2010) [3] R. Musat, S. Moreau, F.

Poidevin, M. H. Mathon, S. Pommeret and J. P. Renault (2010) Phys. Chem. Chem. Phys., 12, 12868 [4] R. Musat, J.P. Renault, M. Candelaresi, D. J. Palmer, S. Le Caër, R. Righini, S. Pommeret,(2008), Angewandte Chem.-Int. Ed. 47(42):8033-8035

Study of random amphiphilic polyanions for molecular encapsulation of water-insoluble compounds

SCHOTT, Marc-alexandre (Institut des Biomolécules Max Mousseron (IBMM) - UMR CNRS 5247) ; DOMURADO, Dominique (Institut des Biomolécules Max Mousseron (IBMM) - UMR CNRS 5247) ; COUDANE, Jean (Institut des Biomolécules Max Mousseron (IBMM) - UMR CNRS 5247) ; BARBAUD, Christel (Laboratoire de Bio-ingénierie de Polymères Cardiovasculaires (LBPC) Institut Galilée, INSERM U698, UP13)

For more than twenty-five years, random amphiphilic polyelectrolytes have been known to enhance the apparent water solubility of highly hydrophobic compounds (1,2). Poly(dimethylmalic acid) (PDMMLA), a degradable polymer, polyanionic at neutral pH, can be easily obtained in a partially hydrophobized form through copolymerization of malolactones with different pendant aliphatic or aromatic groups (3,4). In this work, we synthesized various malolactones to obtain a range of amphiphilic copolymers with varying hydrophobic substituent rate and chain length. The influence of these parameters, of pH and of the presence of sodium chloride upon the apparent solubility of pyrene and clofazimine in aqueous solutions of these polymers was studied.

References : (1) J. Huguet et al., J. Controlled Release, 1985, 1, 217. (2) I. Hernandez-Valdepeña, et al., Eur. J. Pharm. Sci., 2009, 36, 345. (3) C. Barbaud et al., Des. Monomers Polym., 2003, 6, 353. (4) C. Barbaud et al., Macromol. Chem. Phys., 2004, 205, 199.

A new model for the stability and mobility of finite colloidal concentration

LOZADA-CASSOU, Marcelo (Molecular Engineering Research Program, Mexican Petroleum Institute) ; MANZANILLA-GRANADOS, Héctor (Molecular Engineering Research Program, Mexican Petroleum Institute)

We discuss the problem of concentrated colloidal dispersions, through a well established many-body physics theory, compare our results with other theoretical approaches in the literature and with computer simulations. New effects are found. In particular we discuss the implications for the colloids electrophoretic mobility.

In the past, theoretical studies of colloidal dispersions, at infinite dilution, have been made through the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, for planar and spherical geometries. For concentrated colloidal dispersions two theoretical approaches have been used: a) The cell Model (CM) and b) Integral equation theories, for an effective Yukawa potential. For infinite dilution and concentrated colloidal dispersions, computer simulations have been made. In the case of concentrated colloidal dispersions, computer simulations are limited to relatively small colloidal particle sizes. Here we study concentrated colloidal dispersions through the well established hypernetted chain/mean spherical approximation integral equations theory (HNC/MSA) theory, for a colloidal primitive model (CPM). In the CPM the colloidal particles are charged hard spheres, immersed in a primitive model electrolyte. Hence, no effective Yukawa potential is assumed, or fixed boundary conditions, as in the cell model. With this HNC/MSA-CPM theory we calculate the radial distribution functions for all the fluid components and, thus, also the z-potential and other functions of interest. We compare our results with the CM, other simpler approaches and computer simulations. Important deviations from the CM results are reported. New effects, attributed to the large size and charge and to the finite concentration of colloidal particles, are found. In particular, the HNC/MSA-CPM theory predicts a polarity inversion of z-potential for several conditions, always associated with charge reversal, whereas none of the other approaches predict such an inversion. However, if different charge distributions on the colloidal particles are considered, polarity inversion of the z-potential may not be observed. We discuss the possible implications of our results in relation to the electrophoretic mobility of colloidal particles, in concentrated colloidal dispersions. An excellent qualitative agreement between our theoretical predictions and our computer simulations is observed.

Role of non-ideality for the ion transport in porous media: derivation of the macroscopic equations using upscaling

MIKELIC, Andro (Université Lyon 1, Institut Camille Jordan)

In this talk we undertake the rigorous upscaling of a system of partial differential equations describing the non-ideal transport of a N-component electrolyte in a dilute Newtonian solvent through a rigid porous medium. The motion is governed by a small static electric field and a small hydrodynamic force, which allows us to use O'Brien's linearized equations as the starting model. We establish convergence of the homogenization procedure and discuss the homogenized equations. Based on the rigorous study of the underlying equations, we prove that the effective tensor satisfies Onsager properties, namely is symmetric positive definite. This result justifies the approach of many authors who use Onsager theory as starting point

Solvation of silver in saline hydrothermal fluids from first-principle molecular dynamics

VUILLEUMIER, Rodolphe (Département de chimie de l'ENS - UPMC) ; JONCHIERE, Romain (UPMC) ; FERLAT, Guillaume (UPMC) ; SAITTA, A. Marco (UPMC) ; SEITSONEN, Ari P. (University of Zürich)

The knowledge of the speciation of coinage metals is a key element of the understanding of their transport in hydrothermal conditions and the formation of metal deposits from geological fluids. In brines, the main carrier of silver, solvated as silver cation Ag+, is the chloride anion Cl-. However, the structure and the stoechiometry of the silver-chloride complexes, crucial for constraining thermodynamical models of Ag+ solubility at high temperature/high pressure, are largely unknown. Here, we will present a first-principle molecular dynamics study of Ag+, Cl- and silver-chloride complexes in water at both ambient and supercritical conditions.

After presenting the description of supercritical water by density functional theory (DFT) based first-principle molecular dynamics, we will present results on the solvation of Ag+, Cl-, AgCl2- and AgCl32- species, both at ambient and supercritical conditions. It is shown that AgCl2- makes a very stable linear complexe, arising from a pseudo-Jahn-Teller effect. Preliminary results indicate that AgCl32- is unstable in supercritical conditions and hardly stable in ambient conditions. When formed at ambient conditions, its structure is that of a linear AgCl2- with the third Cl-pushed away in the solvation shell of the complex. Simulation results will be compared with new x-ray absorption experiments.

Zeta potential, surface properties and flocculation behaviour of colloidal clay

CHASSAGNE, Claire (TU Delft)

The so-called zeta potential is by definition the electric potential at the shear (or slip) plane of an interfacial double layer. Any charged surface in an electrolyte suspension can therefore be attributed a zeta potential (or, correspondingly, an electrical charge at the plane of shear).

The electrostatic interactions between particles are dependent on their zeta potential. Since these interactions determine the ability of a suspension to remain stable or to flocculate, the zeta potential is widely used as a practical tool to determine the stability of a colloidal suspension. The applications are numerous, from food industry, medical science to soil engineering.

First, the conversion of the measured data into zeta potentials will be presented. We will discuss the available numerical and analytical formulae for the case of spheres for all ionic strengths, surface charges and particle radii. We will show the importance of analyzing two independent electrokinetic experiments in order to assess correctly all of the system's parameters, as the value of the zetpotential a can be greatly influenced by the particle's surface (Stern layer) properties which adds at least one unknown in the set of equations.

Very limited theoretical results are available for non-spherical particles. We were able to derive a (simple) theoretical formula for the case of spheroidal particles. This formula has successfully been used in the interpretation of electrophoretic mobility data obtained from clayey suspensions.

In particular it reconciles the zeta potential values with the observed flocculation behaviour at different pH's and ionic strengths.

References:
C. Chassagne, F. Mietta and J.C. Winterwerp Electrokinetic study of kaolinite suspensions Journal of Colloid and Interface Science, 336, 352 - 359, 2009
C. Chassagne and D. Bedeaux The dielectric response of a colloid spheroid Journal of Colloid and Interface Science 326, 240-253, 2008

Molecular Density Functional Theory of Solvation: From polar solvents to water

BORGIS, Daniel (Laboratoire PASTEUR, UMR 8640, CNRS-ENS-UPMC) ; LEVESQUE, Maximilien (Laboratoire PASTEUR, UMR 8640, CNRS-ENS-UPMC) ; ZHAO, Shuangliang (Laboratoire PASTEUR, UMR 8640, CNRS-ENS-UPMC) ; VUILLEUMIER, Rodolphe (Laboratoire PASTEUR, UMR 8640, CNRS-ENS-UPMC)

A classical density functional theory approach to solvation in molecular solvent is presented. The solvation properties of an arbitrary solute in a given solvent, both described by a molecular force field, can be obtained by minimization of a position and orientation-dependent free-energy density functional. In the homogeneous reference fluid approximation, limited to two-body correlations, the unknown excess term of the functional approximated by the angular-dependent direct correlation function of the pure solvent. We show that this function can be extracted from a preliminary MD simulation of the pure solvent by computing the angular-dependent pair distribution function and solving subsequently the Molecular Ornstein-Zernike equation using a discrete angular representation. The corresponding functional can then be minimized in the presence of an arbitrary solute on a three-dimensional cubic grid for positions and Gauss-Legendre angular grid for orientations to provide the solvation structure and free- energy. This two-step procedure is proved to be much more efficient than direct molecular dynamics simulations combined to thermodynamic integration schemes. The approach is shown to be relevant and accurate for prototype polar solvents such as the Stockmayer solvent or acetonitrile. For water, although correct for neutral or moderately charged solute, it tends to underestimate the tetrahedral solvation structure around H-bonded solutes, such as spherical ions. This can be corrected by introducing suitable three-body correlation terms that restore both an accurate hydration structure and a satisfactory energetics. Applications to the hydration of atomistically-resolved clay surfaces will be presented. References

Effect of long-range interactions on ion equilibria in liquid-liquid extraction

ZEMB, Thomas ; DUFRECHE, Jean-François
Institut de Chimie Séeparative de Marcoule ICSM, UMR 5257 CEA / CNRS / Université de Montpellier 2 / ENSCM, Centre de Marcoule - Bât. 426 BP 17171, 30207 Bagnols sur Ceze Cedex France

We demonstrate here that equilibria of electrolytes between a solvent phase containing amphiphilic extractants and salts are not only dependent on complexation towards nearest neighbors but also on all other long range supramolecular interactions. Taking into account bulk, polarization and chain reorganization terms, we show the net free energy difference associated to one ion pair transfer from water can depend by more than 50\% on long range interactions dominating complexation. Selectivity i.e. the free energy difference for two ion pairs- can originate not from a direct complexation difference, but by supramolecular effects linked to microstructural changes associated to ion transfer.

Towards a simple theory of the viscosity of electrolyte solutions: a mode-coupling approach

MOLINA, John J., DUFRECHE, Jean-François, TURQ, Pierre

The transport of ions in electrolyte solutions has remained an active area of research for almost a century. Although explicit solvent computer simulations have proven to be a valuable tool in the study of such phenomena, their complexity has always favored the use of continuous solvent models. The first such models where obtained in the 1930's through the pioneering works of Debye, Hu¨ckel, and Onsager[1], who managed to provide a correct explanation for the rise in the self-diffusion, conductivity, and viscosity of electrolyte solutions as a function of the salt concentration. Unfortunately, these limiting laws are only useful for very dilute solutions, typically up to millimolar concentrations. While similar continuous solvent models[2], which are valid at molar concentrations, have been developed for the self- and mutual-diffusion, as well as the conductivity, no such theory has been proposed for the viscosity of electrolyte solutions. As with all the ion thermodynamic and dynamic properties, the Fuoss- Falkenhagen Limiting Law predicts that the ionic (excess) viscosity should be proportional to the square-root of the concentration. However, at moderate concentrations, experiments show that the dominant contribution is linear with the concentration. Up to now, no precise model has been found for this linear term (the Jones-Dole B coefficient), which is able to explain the high salt-specificity observed experimentally[3]. In particular, all models proposed so far predict an increase in the viscosity (corresponding to a positive value of B); whereas experimentally, this B coefficient can be both positive (Li-Cl and Na-Cl) or negative (K-Cl). Although the Einstein relation for the viscosity of (neutral) colloids allows for a change in sign of the B coefficient (depending on the sign of the partial molar volumes)[4], when it is applied to electrolyte solutions, the correction is seen to go in the wrong direction. The first step towards providing a microscopic theory for the viscosity of electrolyte solutions was taken by Chandra and Bagchi[5], who were able to recover the exact Fuoss-Falkenhagen limiting law using a Mode-Coupling calculation[6]. We extend their work to take into account the effect of the ion-solvent interactions, which are understood to be at the origin of the anomalous behaviour of the B coefficient (usually explained on the basis the structure-making or structure-breaking nature of the ions). We have used Molecular Dynamics simulations to study the variation of the water structure as a function of the salt concentration, in order to compute the corresponding contributions to the viscosity. To first order, we find that the (long-time) water-water correlations provide a negative contribution to the viscosity, while the ion-ion contribution is always positive, and the ion-water contribution can be ignored. The relative importance of these different terms, together with the short-time binary collision term, will gives rise to the highly salt-specific B coefficient.

References

[1] L. Onsager and R. M. Fuoss. *JCP*, 36(11):2689–2778, 1932.
[2] J.-F. Dufrêche et al. *JPCB*, 109(20):9873–9884, 2005.
[3] Y. Marcus. Ion solvation. John Wiley & Sons, 1985.
[4] A. Einstein. Annalen der Physik, 339(3):591–592, 1911.
[5] A. Chandra and B. Bagchi. *JCP*, 113(8):3226, 2000.
[6] U. and M. Zoppi. Dynamics of the Liquid State. Oxford University Press, 2003.

High temperature solubility of lanthanide halides in alkali metal halide melts.

GAUNE-ESCARD, Marcelle[1], RYCERZ, Leszek[2], GADZURIC, Slobodan[3]
[1]Ecole Polytechnique, CNRS UMR 6595, Marseille, France
[2] Chemical Metallurgy Group, Technical University, Wroclaw, Poland
[3] Dpt Chemistry, University of Novi Sad, Novi Sad, Serbia

Phase equilibria in lanthanide-alkali halide melts are generally complex and characterized by the existence of several stoichiometric compounds of various stability. The ionic radii (r_i) and/or charges (e_i) as also their combination, called "ionic potential" $IP = e_i/r_i$, where $e_i = Z_i\varepsilon$ (Z_i = valency, ε = elementary charge), were found to be important parameters. Lanthanide halides are generally trivalent at high temperature and efforts were performed to screen the LnX_3-MX phase diagrams according to the $IP(M^+)/IP(Ln^{3+})$ ratio. This classification was tested on the $CeBr_3$-MBr binary systems (M=Li, Na, K, Rb, Cs), still unknown at that time. Further experimental investigations validated the predicted phase diagram topology.

A similar approach was conducted on the LnX_2-MX mixtures, which are of industrial interest. Experimental data were available on 45 different systems (fluoride melts were not considered in this work). This presentation will highlight how their phase equilibrium features can also be analyzed in terms of $IP(M^+)/IP(Ln^{2+})$ evolution.

Understanding radionuclide chemistry and transport in clay-rich materials - a key element for demonstrating the safety of underground disposal facilities in clay-rock formations

ALTMANN, Scott, Andra, R&D Division, 1, rue Jean-Monnet, Châtenay-Malabry, FR

Disposal of radioactive waste deep underground in clay-mineral rich formations has been selected by several countries (France, Belgium, Switzerland.), principally because of their very low permeabilities and demonstrated capacities to retard migration of most radionuclides by sorption. Among the key phenomena which must be understood in order to demonstrate the long term safety of these facilities are (i) radioelement chemistry (redox state, solution speciation, sorption at mineral interfaces) and (ii) diffusion-driven transport. Much research has, and is, being carried out by international scientific community regarding these aspects, much of it involving directly or indirectly the solution and interfacial chemistry of radioelements. Of particular importance are efforts (i) to improve the quality and comprehensiveness of thermodynamic data bases, (ii) to properly evaluate the composition of clayrock pore solutions and (iii) to understand the phenomena controlling radionuclide speciation and mobility in saturated clay-rich materials. This talk presents a brief overview of the state of progress regarding these aspects and future perspectives.

A novel concept for augmented van der Waals equation of state

TROKHYMCHUK, Andrij[1], MELNYK, Roman[1], NEZBEDA, Ivo[2], [1] Inst. Condensed Matter Phys., Ukraine Acad. Sci., Lviv, Ukraine, [2]Faculty of Science, J.E. Purkinje Univ., Usti n. L., Czech Republic

The commonly used augmented van der Waals (vdW) equations are based on the hard sphere(hard body) primary contribution to the properties of fluids and makes use of availability of a number of analytic results for their properties. Nonetheless, this choice suffers from two defects: (i) inaccuracy when only one simple correction term is used, and (ii) limitation to ambient and not too much elevated temperature range only. As an attempt to remove these drawbacks we have recently formulated an expansion (augmented vdW EOS) about a reference system with soft interactions which, within the spirit of a unified view of fluids, incorporates also the attractive interaction at short separations.

The proposed approach is based on a short range Yukawa reference and the knowledge of the Yukawa fluid properties and its flexibility. The methodology of the approach will be formulated and then its implementation for the three most important simple fluids, the Sutherland, Lennard-Jones, and EXP6 fluids, will be presented. Particularly, the application of the method to the EXP6 fluids extends the applicability of augmented vdW equations to the region of supercritical conditions and very high pressures, i.e. the region where a special theoretical treatment is required and the available results are either only in a numerical form or represent only empirical correlations.

The presented results clearly show that the suggested approach may provide a simple and yet quite accurate augmented vdW equation in an analytic form able to perform over a very large range of thermodynamic conditions.

Poster Abstracts

The influence of ionic strength on the equilibrium constant of vanadyl(IV), O-S anionic ligand of D-penicillamine

HAKIMELAHI, Rakhshan (Department of Chemistry, Jahrom Branch, Islamic Azad University, Jahrom, Iran)

The presence of vanadium-sulfur bonding has been found to form stable complexes and exhibit high insulin mimetic activity . It has been found that the effectiveness of the anchoring donors in coordination follows the sequence: Phenolate-O- >/alcoholate-O-> thiolate-S->/carboxylate-COO->/NH2 .In the present study we have measured the concentration formation constant for the 1:2 complex of vanadyl(IV) and D-Penicillamine in aquas solution at 25oC.

Reaction of D-H2Pen and VO(acac)2 at pH=10 lead to the formation of [VO(Pen)2]2- Thermodynamic stabilities have been studied using UV/Vis spectrophotometry and SQUAD program. This program is designed to calculate the best values for the stability constants of the proposed equilibrium model by employing a non-linear least square approach.The results showed that the best fitting corresponds to 2 : 1 complex model and coordination sites were thiolate and carboxylate. This reaction is an exothermic process and the changes of entropy is negative . D-Penicillamine is able to release H of S-H , since thiolate ion is more active than amine group to coordinate to vanadyl ion, so the produced vanadyl complex is VO(S2O2) coordination mode. Because of formation more ions in products than source materials in the equilibrium, Kγ decreases and KC increases up to 0.1 ionic strength.

Content :

1. Introduction The coordination chemistry of vanadium with sulfurcontaining ligands is an emerging field of interest with relevance to several disparate biological systems [1-4]. The presence of vanadium-sulfur bonding has been found to form stable complexes and exhibit high insulin mimetic activity [5]. It has been found that the effectiveness of the anchoring donors in coordination follows the sequence: Phenolate-O- >/alcoholate-O-> thiolate-S->/carboxylate-COO->/NH2 [6]. In the present study we have measured the concentration formation constant for the 1:2 complex of vanadyl(IV) and D-Penicillamine in aquas solution has been measured as a function of ionic strength by spectrophotometry at 25oC. 2. Methods The absorption spectra were recorded by shimadzu 1650 spectrophotometer using 1 cm quartz cuvettes,with thermostated cell compartment. Titrations were carried out by adding 50µl aliquots portions of a solution of D-penicillamine directly into the quartz cell containing VO(acac)2. The titration experiments were continued untill the absorbance of the VO(acac)2 solution in the UV-Vis range remained constant. The spectra were recorded in the range of 500 to 900 nm at pH=10 and different temperatures(20,25,30,35,40,45oC)in pure water and different ionic strengths (0.05, 0.1, 0.15, 0.2, 0.4, 0.6, 0.8) of KCl. Our results at 25oC showed that there was an upright relationship between

KC and ionic strength up to 0.1 ionic strength and an inverse relationship in superior ionic strengths. 3. Results and Discussion Reaction of D-H2Pen and VO(acac)2 at pH=10 lead to the formation of [VO(Pen)2]2-. Thermodynamic stabilities have been studied using UV/Vis spectrophotometry and SQUAD program. This program is designed to calculate the best values for the stability constants of the proposed equilibrium model by employing a non-linear least square approach.The results show that the best fitting corresponds to 2 : 1 complex model and coordination sites are thiolate and carboxylate. This reaction is an exothermic process and the changes of entropy is negative .
The equilibrium of VO(acac)2: D-H2Pen can be conveniently characterized by three familiar thermodynamic parameters: standard Gibbs free energy , ΔG°, enthalpy, ΔH° , and entropy, ΔS° changes. Furthermore concentration formation constant (Kc) as a function of (μ)1/2 shows that Kc increases up to 0.1 ionic strength and then decreases . These changes show that the reaction leads to constitute more ions in products.

4. Conclusion D-Penicillamine is able to release H of S-H , since thiolate ion is more active than amine group to coordinate to vanadyl ion, so the produced vanadyl complex is VO(S2O2) coordination mode. Because of formation more ions in products than source materials in the equilibrium, Kγ decreases and KC increases up to 0.1 ionic strength.

Keywords: Penicillamine, VO(acac)2, SQUAD, Ionic strength, Thermodynamic Parameters 5.

References [1] K.H. Thompson and C. Orvig,. Coord. Chem. Rev. 1033, 219-221(2001) [2] D. Rehder,. Coord. Chem. Rev. 182, 297-322(1999) [3] A. Butler and J.V. Walker, Chem. Rev., 93, 1937-1944(1993) [4] D. C. Crans, J. J. Smee, E. Gaidamauskas, L.Yang, Chem. Rev. 104, 849-904 (2004) [5] K. H. Thompson and C. Orvig, Met. Ions Biol. Syst, 41, 221-252(2004) [6] T. Kiss, T. Jakusch, J.C. Pessoa , L. Tomaz,.Coor. Chem. Rev. 237, 123-133(2003)

Toward fragment-based drug design using a new ligand-mapping method based on molecular liquid theory

IMAI, Takashi (RIKEN) HIRATA, Fumio (Institue for Molecular Science) ; SUGITA, Yuji (RIKEN)

Fragment-based drug design (FBDD) is a recently emerging approach which can provide an effective starting point in the discovery of new drug compounds. In FBDD, a series of drug fragments is first screened and then a few active fragments are linked or merged to construct a much more active lead compound. FBDD has the advantage that only a limited number of compounds have to be examined because the variety can be realized by the combination; on the other hand, it has the drawback that the fragmentation can reduce the binding affinity to make it more difficult to detect the binding modes. Recently, we proposed a new computational method for ligand mapping on protein surfaces (3D-RISM-LM) based on the molecular theory of solvation known as 3D- RISM. In the method, ligand is regarded as a solvent and the 3D-spatial distribution functions of ligand atomic sites are used to identify the most probable binding modes

(MPBMs) of ligand molecule. In this study, 3D-RISM-LM is applied to FK506-binding protein to demonstrate the usefulness of the method. In the calculation, the MPBMs of several fragments that correspond to functional moieties of the known inhibitors are obtained. On the basis of the results, we discuss the practical ability of FBDD using 3D-RISM-LM. Discussion includes whether the fragment MPBMs can identify the inhibitor-binding sites, whether linking and/or merging of them can reproduce the known inhibitors, particularly the common anchor motif, and whether they can predict the effective direction of fragment growth.

The influence of anthropogenic drainage waters on adjacent area soil composition

NOVIKOVA, Svetlana (Novosibirsk State University, Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences) ; GASKOVA, Olga (Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences)

Belovsky Zinc Plant (Kemerovo Region, Russia) processed sphalerite concentrate using pyrometallurgical method to extract zinc. After the plant had stopped working, nearly 1 million ton of wastes as clinker heap of 15 m height were accumulated. The chemical, mineralogical composition of clinkers and hydrochemistry of the drainage waters were studied in detail. It was found that Zn goes into solution from solid waste more intensively than Cu, then secondary Cu phases precipitate in the ditch and settling pond. The target of this research is to analyze heavy metal species in environmental soils. Soil samples were collected at the three sites with irregular pollution: 200 m from the plant, behind the settling pond near the river and in background-one. The acidity of soil aqueous extracts, organic carbon concentration, total metal contents and their distribution in the solid species were determined. Of particular interest is the discussion of soil contamination by Zn and Cu as the major pollutants, Fe, Mn and Ca as the basic natural/anthropogenic cations. Our results indicate that Zn is a predominant soil contaminator. The clay distant soil is the most effective geochemical barrier, which accumulates Zn, Mn, Cu, Ni related with the amorphous Fe and Mn hydroxides.

Hydrophobic effect on the conformational equilibria of diethyl ether and ethyl isopropyl ether using Raman spectroscopy and molecular dynamic simulation

WADA, Ryoichi (Graduate School of Science and Engineering Ritsumeikan University) ;KASEZAWA, Kunihiro (Graduate School of Science and Engineering Ritsumeikan University) ; KATO, Minoru (Graduate School of Science and Engineering and College of Pharmaceutical Sciences Ritsumeikan University)

Hydrophobic effect on a conformational equilibrium of molecule is an important factor for the stability of protein's structure. In this study, we have investigated the solvent effect of water on the conformational equilibria of diethyl ether (DEE) and ethyl isopropyl ether (EIE) as model molecules, which have different size of hydrophobic groups each other, using Raman spectroscopy and molecular dynamic simulation.

Raman spectrum of DEE in neat liquid at 298.2 K shows the bands at 440 cm-1 and 500 cm-1 which are assigned to the COC bending mode of the trans-trans (tt) and trans- gauche (tg) conformers, respectively. From the intensities of the bands and their temperature and pressure dependencies, the free energy, enthalpy, entropy and volume difference between the tt and tg conformers in water and organic solvents were determined. The values for EIE were also determined in a similar manner.

In the organic solvents, the solvent effects on thermodynamic quantities of DEE and EIE were similar to each other. On the other hand, in water, the entropic term of EIE was significantly lager than those of DEE. The tg conformers of the ether molecules are stabilized by the entropic term. This behavior is consistent with the picture of dehydration of hydrophobic molecule. Our molecular dynamic simulation indicated that the coordinate number of water around ethyl group of the tg conformers are smaller than that of the tt conformers, and the number of dehydrated water molecules of EIE are larger than that of DEE. This result is consistent with the thermodynamics from Raman spectroscopy.

Transference Number and Conductance Studies of Sodium Chloride in 20 Mass per cent Ethanol + Water, and 20 Mass per cent Formamide + Water Mixture at 298.15 K

TOMAš, Renato (Faculty of Chemistry and Technology, University of Split) ; SOKOL, Vesna (Faculty of Chemistry and Technology, University of Split) ; BOšKOVIć, Perica (Faculty of Chemistry and Technology, University of Split)

Transference numbers of sodium chloride were determined at 298.15 K from the potential difference (pd) measurements of the cell with liquid junction [1]: Ag(s)/AgCl(s)/NaCl (Z, m1)/NaCl (Z, m2)/AgCl(s)/Ag(s), at various salt molalities (m1 > m2) in 20 mass. % mixture (Z) of ethanol or formamide with water by using literature date for the activity coefficient [2,3]; two organic solvents influence the mixture permitivity inversly. Molar conductivities of NaCl were determined in both mixtures and treated by the Lee-Wheaton equation to obtain their limiting value (Lo). Limiting transference number (to) of the sodium ion, obtained by extrapolation to zero-molality, serves to derive ionic conductivities (lo+, lo–) from Lo. Results are compared with that in similar systems and discussed.

References:

[1] B. M. Braun, H. Weingärtner, J. Solution Chem., 14 (1985) 675. [2] M. A. Esteso, O. M. Gonzalez-Diaz, F. F. Hernandez-Luis, L. Fernandez-Merida, J. Solution Chem., 18 (1989) 277. [3] F. Hernandez-Luis, H. R. Galleguillos, L. Fernandez-Merida, O. Gonzalez-Diaz, Fluid Phase Equilib., 275 (2009) 116.

Experimental study of regulariries in the rare earths hydrolytic behaviour

STEPANCHIKOVA, Sophia (Alexandrovna) BITEYKINA, Raisa (Petrovna)

Rare earth elements are of great importance in geochemical researches. Data on their complex stability as function of atomic number provide information on physico- chemical properties of REE, responsible for their migration into natural waters, fractionating from mineraloforming fluids and accumulation in solid phases. Among all the REE equilibria in natural waters, environmental and geochemical systems hydrolysis equilibria are the least well understood. Measured values of the stability constants have significant dispersion and being obtained in different experimental conditions, are often incomparable with each other. The experimental data are usually obtained at considerably ionic strength and no taking in account the possible presence in solutions, together with monohydroxides, higher-order complex species. The main goal of this study was to minimize the errors arising from extrapolation of stability constants to zero ionic strength. Equilibriua in near-neutral and alkaline aqueous solutions of REE series were examined using spectrophotometric method with m-cresol purple and 2-naphtol as pH indicators with intensive specific spectra in visible and UV regions. Experiments have been obtained at ionic strength no more 0.0005 at pH measured with a great accuracy without of polymer forms, side reactions and hydroxide precipitations. They were based on the standardized extinctions and ionization constants of indicators.

Complex anions as Ln(OH), Ln(OH)2 and Ln(OH)3 have been found in freshly prepared LnCl3 solutions. Species as Ln(OH)4 have also been detected for same of yttrium group elements. The hydroxide complexes stability constants at zero ionic strength were obtained as parameters of linear regression characterized spectra of indicators in the solutions under study. On the whole, the data confirm increasing of monohydrixide complexes stability in the direction from La to Lu according to concept of "lanthanoide compression". At the same time failure of monotonous dependence from atomic number is distinctly expressed and is explained by the ligand field and covalence effects. One another set of data suggesting that the chemical bonding in lanthanide complexes is not purely ionic is thus presented.

Stepwise formation of the molecular complexes of 3-nitrofluoranthene with toluene in cyclohexane

KOBAYASHI, Michio (Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama Gakuin University) ; HAYASHI, Yoshiyuki (Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama Gakuin

University) ; SHIBUYA, Soutarou (Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama Gakuin University)

The electronic absorption spectra of 3-nitrofluoranthene (NF) in the cyclohexane- toluene mixed solvent showed three different kinds of isosbestic points for the variation in toluene (T) concentration. This observation indicates that NF forms stepwise 1:1(C1), 1:2(C2), and 1:3(C3) molecular complexes with T. The equilibrium constants, enthalpy changes, and entropy changes for NF+T↔C1, C1+T↔C2, and C2+T↔C3 stepwise complex formations have been spectroscopically evaluated. These evaluated data indicate that the relative difficulty in forming the molecular complex is controlled by entropy while the driving force for the molecular complex formation is governed by enthalpy. It is, therefore, spectroscopically demonstrated that the higher the aggregation number, the larger the decrease in entropy and hence the larger the difficulty in forming the aggregate. It has been further observed for stepwise aggregation of NF with T in cyclohexane that the 0-0 band of the first electronic transition band of NF is monotonously weakened and red-shifted with increasing aggregation number. Based on this observation along with the spectroscopically evaluated result that the the enthalpy change for C1 stepwise complex formation is nearly equal to that for C2, three-step aggregation models have been proposed and analysed by an exciton model.

Photo-induced Electron Transfer Reaction between Aromatic Compounds in Ethylene Glycol

INADA, Taeko (Kitasato University) ; TOSAKI, Shyuhei (Kitasato University) ; IKEDA, Hiroshi (Osaka Prefecture University) ; KIKUCHI, Koichi (Tohoku Fukushi University)

Electron transfer (ET) reaction is one of the most important reactions in chemistry and biology. In this works, to make clear the effects of solvent viscosity on photo- induced ET reactions, the ET fluorescence quenching of aromatic compounds and the following ET reactions within the geminate radical pair were studied in ethylene glycol, using aromatic compounds as neutral quenchers, and viologen derivatives as cationic quenchers. On analysis of the free energy change (ΔG) dependence of the rate constant of fluorescence quenching, the reaction distance, and the free radical yield, and the triplet yield in fluorescence quenching, it was found that the switchover of fluorescence quenching mechanism occurs at $\Delta G = -0.25$ eV: the fluorescence quenching is induced by an exciplex formation at $\Delta G > -0.25$ eV and by a long-distance ET at $\Delta G < -0.25$ eV. The shift of switchover ΔG from -0.5 eV for acetonitrile, and methanol, can be explained by the difference in the rate constant of diffusion, and the reaction distance on back ET. Furthermore it was found that ΔG dependence of the rate constant of back ET, and of free radical recombination is interpreted by the Marcus theory as well as the results in acetonitrile, and methanol.

Shape changes in polysorbate 20 micelles of nanoscale self-assembly in aqueous solutions of each of three polar solvents (1,4-dioxane, dimethyl sulfoxide, N,N-dimethylformamide).

AIZAWA, Hideki (Faculty of Pharmaceutical Sciences, Setsunan University

Nanoscale structures of surfactant micelles are much received influences on properties of solvent. Polar solvents dissolve in both water and organic solvents. Clarifications of how their shapes change in aqueous solutions increasing concentration of each of polar solvents therefore attract great attention. In this study, we studied how the shapes of the surfactant polysorbate 20 micelles change in aqueous solutions increasing concentration of each of three polar solvents [0–40% 1,4-dioxane, 0–40% dimethyl sulfoxide(DMSO), 0–60% N,N-dimethylformamide (DMF)] by means of small-angle X-ray scattering. In 100% water, Polysorbate 20 formed core–shell cylindrical micelles. In aqueous solutions increasing the concentration of 1,4-dioxane, the micelles changed from core–shell cylindrical micelles to core–shell discus micelles between concentrations of 10–20% 1,4-dioxane, and then from core–shell discus micelles to core–shell elliptic discus micelles between concentrations of 30–40% 1,4-dioxane. In those solutions of DMSO, they changed from core–shell cylindrical micelles to core–shell discus micelles between concentrations of 0–10% DMSO. In those solutions of DMF, they changed from core–shell cylindrical micelles to core–shell discus micelles between concentrations of 30 –40% DMF. Properties of the polar solvents affected the polar solvent concentration-dependent changes in the shape of micelles.

The anion influence on hydrophobic hydration of tetraalkylammonium hydroxides and salts

LYASHCHENKO, Andrey (Kurnakov Institute of General and Inorganic Chemistry RAS) ; LILEEV, Alexander (Kurnakov Institute of General and Inorganic Chemistry RAS) ; KOBELEV, Alexey (Kurnakov Institute of General and Inorganic Chemistry RAS) ; ALADKO, Ludmila (Kurnakov Institute of General and Inorganic Chemistry RAS)

The research of molecular-kinetic aspects of ion hydration in TAA compound solutions were carried out by the microwave dielectric spectroscopy (11 systems). The measurements of the dielectric permittivity and losses were fulfilled by the method of thin cylindrical rode in a waveguide at frequency range 7.5-25GHz that corresponds to the area of water dielectric permittivity dispersion. We used this method for systematic investigation at temperatures 288-323K or 288-308K. The low-frequency (1 kHz) specific conductivity was measured to calculate ionic losses. In most cases the dipole losses make the basic contribution to total losses, unlike the aqueous solutions with hydrophilic hydration of ions. Cole-Cole relaxation model was used to calculate static dielectric permittivity and dielectric relaxation time in studied systems. Using the Eyring theory of absolute reaction rates the values of activation enthalpy and entropy of dielectric relaxation process were calculated. This values increase in the solutions of TAA salts and hydroxides. The basic difference of the specified solutions from systems with hydrophilic hydration of ions consists in reduction of water mobility in hydration shells of ions. Molecular-kinetic properties of aqueous solutions were compared at the transition from hydrophilic hydration of cation and anion (potassium formate and hydroxide solutions) to hydrophobic hydration of cation and hydrophilic hydration of anion (tetramethylammonium hydroxide, tetrabutylammonium hydroxide and tetrabutylammonium fluoride), further to hydrophobic hydration of cation and anion (tetrabutylammonium acetate, propionate, butyrate and valerianate). The increase of nonpolar group number for cations and anions causes the above-mentioned changes. The temperature effects of hydrophobic hydration for solutions of TAA compounds are considered. The research of molecular-kinetic aspects of ion hydration in TAA compound solutions were carried out by the microwave dielectric spectroscopy (11 systems). The measurements of the dielectric permittivity and losses were fulfilled by the method of thin cylindrical rode in a waveguide at frequency range 7.5-25GHz that corresponds to the area of water dielectric permittivity dispersion. We used this method for systematic investigation at temperatures 288-323K or 288-308K. The low-frequency (1 kHz) specific conductivity was measured to calculate ionic losses. In most cases the dipole losses make the basic contribution to total losses, unlike the aqueous solutions with hydrophilic hydration of ions. Cole-Cole relaxation model was used to calculate static dielectric permittivity and dielectric relaxation time in studied systems. Using the Eyring theory of absolute reaction rates the values of activation enthalpy and entropy of dielectric relaxation process were calculated. This values increase in the solutions of TAA salts and hydroxides. The basic difference of the specified solutions from systems with hydrophilic hydration of ions consists in reduction of water mobility in hydration shells of ions. Molecular-kinetic properties of aqueous solutions were compared at the transition from hydrophilic hydration of cation and anion (potassium formate and hydroxide solutions) to hydrophobic hydration of cation and hydrophilic hydration of anion (tetramethylammonium hydroxide, tetrabutylammonium hydroxide and tetrabutylammonium fluoride), further to hydrophobic hydration of cation and anion (tetrabutylammonium acetate, propionate, butyrate and valerianate). The increase of nonpolar group number for cations and anions causes the above-mentioned changes. The temperature effects of hydrophobic hydration for solutions of TAA compounds are considered. Change of molecular-kinetic mobility of water molecules in a solution is summary characteristic of cation and anion hydrations. The parting scheme of water mobility effects and detection of the cation and anion individual contributions is suggested. The relation between the solubility diagrams of the clathrate TAA compounds with the hydrophobic hydration of its ions in the solutions is established. Supersaturated and nonsaturated solutions have no the special distinct molecular-kinetic properties. It is supposed that hydrophobic hydration in solutions of TAA hydroxides and salts near its melting temperature determines the formation of clathrate hydrates in these systems.

This work was supported by the Programs of the Russian Academy of Science.

Complexation of protactinium(V) with citric and nitrilotriacetic acids

LEGUAY, Sébastien (CNRS, Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex) ; LE NAOUR, Claire (CNRS, Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex) ; AUPIAIS, Jean (CEA, DAM, DIF F-91297 Arpajon, France) ; JEANSON, Aurélie (CNRS, Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex) ; HAMADI, Sena (CNRS, Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex) ; DEN AUWER, Christophe (CEA, DEN, Marcoule BP 17171, 30207 Bagnols sur Ceze, France) ; ROQUES, Jerome (CNRS, Université Paris-Sud, IPNO, 15 Rue Georges Clémenceau, 91406 Orsay Cédex) ; MOISY, Philippe (CEA, DEN, Marcoule BP 17171, 30207 Bagnols sur Ceze, France)

The possible use of thorium as nuclear fuel for energy production has led to a renewal of interest on the physical-chemical properties of protactinium. This element will namely be produced as isotopes 233Pa and 231Pa in thorium-based fuel reactor. Structural and thermodynamic data relative to protactinium species in presence of various ligands are essential for modelling the behaviour of the element in environmental and biological media. The present work focuses on the complexation of Pa(V) with citric and nitrilotriacetic acids in acidic medium. In order to bypass the strong tendency of protactinium towards polymerization, thermodynamic data (complexation constants) are determined using liquid-liquid extraction with the element at tracer scale (CPa < 10-10M). The charge of complexes of maximum order is deduced from CE-ICP-MS. X-ray absorption spectra are registered on a sample of Pa(V) citric acid in order to get information about the occurrence of the mono-oxo bond, the distances Pa-ligand and the geometry of the complexe.

Acknowledgements This work was supported by PACEN/GNR PARIS (French Organization). The authors greatly acknowledge Marc Lecomte (CEA-LABRA) for providing the thorium irradiation at the Osiris reactor of CEA Saclay (France).

Interparticle Interactions from Activity of Water of Ternary Amino Acid-Electrolyte Solutions

TSURKO, Elena Nikolayevna (Research Institute of Chemistry, Karasin National University, Svoboda Sq.4, 61022 Kharkiv, Ukraine) ; NEUEDER, Roland (Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitaetsstr. 31, 93053 Regensburg, Germany) ; MüLLER, Rainer (Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitaetsstr. 31, 93053 Regensburg, Germany) ; KUNZ, Werner (Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitaetsstr. 31, 93053 Regensburg, Germany)

Ions specifically interact with macromolecules such as proteins and therefore can influence important biological functions like protein solubility and stability, protein-protein interactions and enzyme activity. The determination of the thermodynamic properties of binary amino acid-water mixtures as well as of ternary amino acid-salt-water mixtures may help to get a deeper insight into the mechanisms underlying these effects which are important for living body function. In this work ion-specific interactions with glycine, which is the smallest proteinogenic amino acid and also an important neurotransmitter, were studied. Vapour pressure osmometry measurements were performed as a function of amino acid or salt concentration at T=298.15 K.

From these measurements the activity and osmotic coefficients have been calculated which are directly related to the chemical potentials of the species and therefore to their free energy. Measurements were undertaken for the system glycine-NaCl-water varying the concentration of glycine and NaCl (msalt=0, 0.5, 1.0, 2.0, 3.0 mol/kg and mAS = 0–3 mol/kg), where mAS is amino acid and msalt electrolyte concentration. Modelling of the thermodynamic properties was performed using the Pitzer equations and considering the Gibbs-Duhem equation for ternary systems containing electrolyte and non-electrolyte. The data are compared with those obtained for more complex ternary systems comprising three-basic amino acids (aspartic or glutamic acid) and salts composed of Na+, K+, Ac-, Cl-, NO3- and SCN-.

Hydration and microwave dielectric properties of alkali metals and ammonium fluorides

LILEEV, Alexander (Moscow State University of Environmental Engineering)
LYASHCHENKO, Andrey (Institute of General and Inorganic Chemistry RAS)

The complex dielectric permittivity for the series of aqueous alkali metals (Na, K, Cs) and ammonium fluoride solutions was investigated in frequency range that corresponds to the maximum of the dielectric permittivity dispersion of water and aqueous electrolyte solutions (7.5-25 GHz). The measurements were made at 288- 308 K in a wide area of salt concentrations. The low-frequency specific electrical conductivity (s) was investigated for calculation of ionic losses. The Cole-Cole relaxation model was used for analyze of frequency dependence of complex dielectric permittivity. Static dielectric constant was determined from the circular diagrams by means of extrapolation to the zero frequency. The reduction of dielectric constant is observed when the salt concentration is increased. It depends from ionic radiuses of cations: when ionic the radius increase from Li to Cs, values of dielectric constant decrease in same order. The temperature coefficient of dielectric constant decreases with the increase of salt concentration and lead to zero at high concentrations.

The values of dielectric relaxation time (t) and activation characteristics: Gibbs energy (ΔG) enthalpy (ΔH), entropy (ΔS). The changes of t values characterize the water molecule mobility in the hydration shells of ions. The values of dielectric relaxation time decrease in comparison with pure water for alkali metals fluoride solutions at all investigated temperatures. It proves the increase of water molecules mobility in solutions under action of the dissolved ions. The decrease of t values is more pronounced at low temperatures when the structure of water in solutions is destroyed by thermal motion of molecules in lesser degree. The values of activation enthalpy reflect the structuredness of H-bond water net in solutions. Its decrease in alkali metals fluoride solutions shows that the structure- breaking effect exists in these solutions. The appositive changes of t and ΔH values are observed for ammonium fluoride solutions. It related with features of structure of ammonium and fluoride ions. These ions can form four tetrahedral H-bonds with H2O molecules without disorder of initial water structure. In ammonium fluoride solutions the values of t and ΔH increase in comparison with pure water. It means that in these solutions the stabilization of water H-bond set is observed. Note that ammonium fluoride is

unique salt that forms the solid solutions in ice. For the first time the stabilization effect established in the case of hydrophilic hydration of ions. The mechanism of this effect considerably differs from ones of hydrophobic hydration of ions with nonpolar groups (alkyl substituted ammonium salts for example).
This work was supported by the grants of Presidium RAS

Sensitive separation and characterization of plants extracts for discovery of new anticancer leaders

IONKOVA, Iliana (Faculty of Pharmacy, Medical University of Sofia) ; MOMEKOV, Georgi (1Faculty of Pharmacy, Medical University of Sofia, Dunav Str. 2, 1000 Sofia, Bulgaria) ; SCHMIDT, Thomas (Institut für Pharmazeutische Biologie und Phytochemie IPBP, Westfälische Wilhelms-Universität Münster, Germany)

The majority of high-valuable plant secondary metabolites are still isolated from wild or cultivated intact plants. Many medicinal plants contain various bioactive secondary metabolites, such as polyphenolic compounds, terpenoids, alkaloids and some other pharmacologically active metabolites, and have been used as pharmaceuticals for several millennia. The lignans are a large and varied group of natural products with highly complex structures and their specific stereochemical requirements (a wide variety of structural types and enantiomeric forms) make the isolation and structure determination difficult. The chemical diversity is even higher since most lignans are chiral compounds. Rapid and high throughput comprehensive chemical screening of natural Linum plants by combing of different HPLC-ESI/MS-MS -UV/DAD lead to the discovery of more than 60 different lignans comprising compounds of the aryltetralin-, arylnaphthalene-, aryldihydronaphthalene-, dibenzylbutyrolactone-, and furofuran types. This includes discovery of minor new active compounds along with de novo structure elucidation. A series of isolated aryltetralin-, arylnaphthalene demonstrated to have in vitro anticancer properties.
ACKNOWLEDGEMENTS: Financial support from Ministry of Education and Science, Sofia, Bulgaria (grant D002-128/2008 I. Ionkova) is acknowledged.

Electrophoretic mobility of some isotopes in aqueous solution at 25 °C and infinite dilution from conductivity data and/or capillary electrophoresis

AUPIAIS, Jean (CEA)

The electrophoretic mobilities of chloride and bromide isotopes in aqueous solution have been evaluated at 25 °C and infinite dilution by analyzing a combination of data obtained by capillary electrophoresis (CE) and conductivity data extracted from the literature over nearly one century. The electrophoretic mobilities are found to be –(79.124 ± 0.020) 10–9 m2V–1s–1 for Cl– and –(80.99 ± 0.04) 10–9 m2V–1s–1 for Br–. Thanks to the capability of capillary electrophoresis to separate isotopes and the re-evaluation of conductivity data, the following values have been found for 35Cl–, 37Cl–, 79Br–, and 81Br– (in 10–9 m2V–1s–1): –(79.18 ± 0.02), –(78.95 ± 0.06), –(81.04 ± 0.04), and –(80.94 ± 0.04). Like hydrogen isotopes, the isotopic effect involving 7Li+ and 6Li+ ions has been detected from conductance measurement of their chloride salts with a high accuracy. The difference of both isotope mobilities allows eliminating the chloride conductance. Therefore, a simple system can be solved based on the isotopic abundance, and the electrophoretic mobility at infinite dilution of the Li element: The following values have been obtained where the lighter isotope present as expected higher mobility: µ0(7Li+) = 40.09 10–9 m2V–1s–1 and µ0(6Li+) = 40.22 10–9 m2V–1s–1.

Critical and limiting fluxes in ultrafiltration using a porous polymeric tubular membrane

BEICHA, Abdellah (université de Jijel- Algerie) ZAAMOUCHE, Radia (université de Jijel-Algerie)

A new procedure for calculating the critical flux was presented. Both the critical and limiting fluxes depend on the cross-flow velocity and the bulk concentration. For bulk concentrations near the critical concentration, the critical flux can be estimated directly. However, for bulk concentrations beyond the critical value, the critical flux value depends strongly on the concentration polarisation. The permeate flux increases linearly with TMP for every velocity, which then level off to a stationary flux value. The constant flux obtained shows increment with increasing velocity.

Hard convex body fluids confined in random porous media: scaled particle theory

HOLOVKO, Myroslav (Institute for Condensed Matter Physics) ;SHMOTOLOKHA, Volodymyr (Institute for Condensed Matter Physics) ; PATSAHAN, Taras (Institute for Condensed Matter Physics) ; DONG, Wei (Ecole Normale Superiere de Lyon)

In this report we present generalization of the scaled particle theory for the description of hard convex body fluids in random porous media. As a result, analytical expressions for the chemical potential and the equation of state of hard convex body fluids in hard convex body and overlapping hard convex body matrices are obtained. The influence of non-spherical shapes of fluid molecules and matrix particles on thermodynamic properties is discussed. The possibilities of mapping properties of fluids in different models of porous media are discussed. It is shown that thermodynamics in different models is nearly identical if the porosity of the porous materials and the mean interface area are set to be equal.

Ionic Association and Solvation of the Ionic Liquid 1-Hexyl-3-Methylimidazolium Chloride in Molecular Solvents Revealed by Vapor Pressure Osmometry, Conductometry, Volumerty and Acoustic Measurements

SADEGHI, Rahmat (University of Kurdistan) EBRAHIMI, Nosaibah (University of Kurdistan)

A systematic study of osmotic coefficient, conductivity, volumetric and acoustic properties of solutions of ionic liquid 1-hexyl-3-methylimidazolium chloride ([C6mim][Cl]) in various molecular solvents has been made at different temperature in order to study of ionic association and solvation behavior of [C6mim][Cl] in different solutions. The experimental measurements of osmotic coefficient at 318.15 K for binary solutions of [C6mim][Cl] in water, methanol, ethanol, 2-propanol and acetonitrile are taken using the vapor pressure osmometry (VPO) method and from which the values of the solvent activity, vapor pressure, activity coefficients and Gibbs free energies are calculated. Precise measurements on electrical conductances of solutions of [C6mim][Cl] in water, methanol, ethanol, 1-propanol, 2-propanol, 1-buthanol and acetonitrile at 293.15, 298.15 and 303.15 K are reported and analyzed with Barthel's low-concentration chemical model (lcCM) to obtain the limiting molar conductivities and association constants of this ionic liquid in the investigated solvents. Strong ion pairing was found for the ionic liquid in 2-propanol, 1-butanol and 1-propanol, whereas ion association in acetonitrile, methanol and ethanol is rather weak and in water the ionic liquid is fully dissociated. In the third part of this work, the apparent molar volumes and isentropic compressibilities of [C6mim][Cl] in water, methanol, ethanol, acetonitrile, 1-propanol, 2-propanol, 1-butanol, ethylene glycol and propylene glycol are obtained at 288.15-313.15 K temperature range at 5 K intervals at atmospheric pressure from the precise measurements of density and sound velocity. The infinite dilution apparent molar volume and isentropic compressibility values of [C6mim][Cl] in the investigated solvents as well as the excess molar volume and isentropic compressibility deviation values of the investigated solutions are determined and their variations with temperature and type of solvents are also studied. The results are interpreted in terms of ion association, ion-dipole interactions and structural factors of the ionic liquid and investigated organic solvents. The ionic liquid is solvated to a different extent by the molecular solvents, and ionic association is affected significantly by ionic solvation.

Conductance of potassium chloride in methanol at high temperatures and pressures up to 473 K and 100 MPa

HOSHINA, Taka-aki (Nihon University, Department of Applied Molecular Chemistry) ; KAJIWARA, Hodaka (Doshisha University, Department of Molecular Chemistry and Biochemistry) ; WATANABE, Toshikazu (Doshisha University, Department of Molecular Chemistry and Biochemistry) ; TSUCHIHASHI, Noriaki (Doshisha University, Department of Molecular Chemistry and Biochemistry) ; UENO, Masakatsu (Doshisha University, Department of Molecular Chemistry and Biochemistry) ; IBUKI, Kazuyasu (Doshisha University, Department of Molecular Chemistry and Biochemistry)

Conductance measurements in extreme conditions such as high temperatures and pressures are important for a better understanding of the ionic transport processes in solution. We here report measurements of molar electrolyte conductances of KCl in methanol at 293-473 K and 0.1-100 MPa. The molar conductances at infinite dilution and the molar association constants were determined form the concentration dependence of the electrolyte conductance. Single ion conductances were estimated with the assumption that the transference number was independent of temperature and pressure. The single ion conductances of the cation and anion increased with increasing temperature and decreased with increasing pressure. The temperature and pressure dependences of the single ion conductances were qualitatively explained by the dielectric friction theory of the continuum model. The association constant increased with increasing temperature and decreased with increasing pressure. The enthalpy and volume changes of association were estimated from the temperature and pressure dependences of the association constant. The enthalpy changes were positive and increased with increasing temperature. At pressures less than 50 MPa, the volume changes were positive and increased with increasing temperature. At higher pressures, the volume change showed no remarkable temperature dependence.

Heats of Mixing in Binary Liquid Alloys of Transition Metals

DUBININ, Nikolay (Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences)

Some years ago, we have developed the procedure for calculating the thermodynamic properties of binary transition-metal liquid alloys [1] on the basis of the Wills- Harrison (WH) model [2]. More recently, in the framework of the WH model the correction due to the non-diagonal coupling (NDC) between d electrons of different atoms was suggested [3]. In the present work, we study an influence of this correction on the thermodynamics of liquid Fe-Co and Fe-Ni alloys in the framework of the calculation formalism developed in Ref. [1]. The heat of mixing and

Helmholtz free energy of mixing are investigated at different component concentrations near melting. It is found that the results obtained agree with experimental data better than ones obtained without the NDC correction for both alloys under consideration. This tendency is more powerful for Fe-Co alloy and less for Fe-Ni.

This work is supported by the Ural Branch of the Russian Academy of Sciences (project 09-T-3-1012) , Federal Agency on Science and Innovations (contract 02.740.11.0641), and Russian Ministry of Science and Education (contract P895).

[1] N.E. Dubinin, L.D. Son, N.A. Vatolin, J. Phys.: Condensed Matter, 20 (2008) 114111 [2] J.M. Wills, W.A. Harrison, Phys. Rev. B, 28 (1983) 4363 [3] N.E. Dubinin, L.D. Son, J.Phys.: Conference Series, in print (2011)

Influence of solution composition on ion binding with heparin and dextran sulphate

BARTCZAK, Martyna (Institute of Applied Radiation Chemstry, Technical University of Lodz) ; HAWLICKA, Ewa (Institute of Applied Radiation Chemstry)

Conductivity of sodium heparinate, lithium heparinate and dextran sulphate sodium salt at 310 K was measured. In order to investigate an influence of the ionic strength the conductivity was determined in solutions NaCl, LiCl, Me4NCl, CaCl2 and MgCl2. Even in dilute solution the presence of polyelectrolyte decreased the mobility of small ions. For 1:1 salts the conductivity increases linearly with the polyelectrolyte concentration, whereas for 2:1 salts (CaCl2 and MgCl2) these relationships consist of two lines with two different slopes. The fraction of the condensed ions was computed. In NaCl and LiCl solutions of heparin the fractions of the condensed counter-ions are different and for Na+ ions this fraction is slightly greater. The observed difference between sodium and lithium salts does not agree with the Manning's theory, what predicts that the α-fractions for the ions having the same charge are equal. As might be expected Ca2+ ions were better bound to heparin than Na+ ions. However the fraction of the uncondensed Ca2+ ions was high and even in very dilute solution it was close to 10%. The determined fractions of the condensed ions yielded the molar conductivities of the ions in solutions of the mixed Na+/Ca2+ and Na+/Mg2+ salts of dextran sulphate.

The Structure in Water-Alcohol Mixtures by Monte Carlo Method

ATAMAS, Nataliya (Kiev Taras Shevchenko University) ATAMAS, Alexander (Kiev Taras Shevchenko University)

As prototype hydrogen-bonding molecules, water and alcohols (ethanol and propanol) both hold special status. Alcohols are the amphiphile-like molecules capable of hydrogen bounding. The amphiphilic character of alcohols as solutes has been observed to affect both the structure of the surrounding water and to promote their aggregation in aqueous solution. The molecular dynamics (MD) and Monte Carlo (MC) simulations have been used as methodologies to obtain information about the behaviour of molecular liquids. In the present work, we report MC simulation results for pure alcohols and water- alcohols mixtures in the isothermal and isobaric ensemble at T=300K and p=1.0atm. From radial distribution functions the analysis of the local structure and energetic of solutions were done. The parameters of hydrogen bonds and the size of first and second hydrations shape ware determined. From energetics and RDF ware analyzed the local structures of solutions.

Temperature effects on reorientational correlation time of water in formamide and N,N-dimethylformamide - water mixtures

OKADA, Masaki (Doshisha university, Faculty of engineering) ; IBUKI, Kazuyasu (Doshisha university, Faculty of engineering) ; UENO, Masakatsu (Doshisha university, Faculty of engineering)

Mixtures of water and organic liquids have been subjects of numerous physico-chemical investigations because of their interesting properties arising from the effect of organic components on the hydrogen-bonded water structure. In this work, we determined the reorientational correlation times (τc) of heavy water in formamide (FA)- heavy water and N,N-dimethylformamide (DMF)- heavy water mixtures from the NMR relaxation time measurements at 5, 10, 25 and 45 °C under atmospheric pressure, and discuss the hydrophilic and hydrophobic interactions between amide and water. FA molecule consists of hydrophilic aldehyde and amino groups while DMF molecule contains hydrophobic methyl groups. In order to support our discussion, we also performed molecular dynamics simulations. The composition dependence of rotational correlation time in FA-water mixtures showed shallow minimum near 10 mol% at 5 and 10°C. At higher temperatures, rotational correlation time monotonously increased with increasing FA content. These results indicate the competition of two effects: one is the weakening of the hydrogen-bonded structure caused by the replacements of water-water hydrogen-bonds by weaker FA-water ones. The other is the effect of strong dipole interactions between water and FA. FA has much larger dipole moment than water. On the other hand, the composition dependence of rotational correlation time in DMF-water mixtures showed a significant increased with a small addition of DMF and then decreased after showing a maximum at 40 mol%. The initial increase in rotational correlation time could be attributed to the strong hydrogen-bonds the between DMF and water molecules, the enhancement of hydrogen-bonds between water molecules by the hydrophobic effects, and the strong dipole interactions between DMF and water. In DMF-rich region, the number of hydrogen-bonds number per water decreased with increasing DMF content, and the correlation time decreased.

An Infrared and Computational Study of Hydrogen Bonding to Uracil Maryam Hajimohammad pour and Earle Waghorne

HAJIMOHAMMADPOUR, Maryam (UCD,Prof Earle Waghorne)

Uracil, one of the nucleic acid pyrimidine bases is present in RNA but not in DNA, where it is replaced by thymine. The principle role of the nucleic acid bases is to provide reversible anchorages, through hydrogen bonding and so exploring these interactions is important in understanding these systems. Preliminary studies of a number of pyrimidine bases and related compounds showed that they are remarkably strong hydrogen acceptors.

Infrared spectroscopy has been used to elucidate the hydrogen bonding to a number of chromophores in aprotic + protic mixed solvents; the technique allows both the numbers of hydrogen bonds formed and the relative populations of differently hydrogen bonded species to be determined. In the case of uracil the analysis is complicated by the presence of the two C=O moieties, both of which contribute to the infrared spectra and both of which may form multiple hydrogen bonds. Thus the infrared measurements were augmented by computational calculations (Density Functional method with B3LYP and the 6-31+G (d,p) basis set) of uracil hydrogen bonded to DMSO through the two N−H protons and up to three water molecules on each of the C=O groups. The results confirm that uracil, in DMSO, is a remarkably strong hydrogen bond acceptor; thus, for example, essentially all of the uracil molecules in a 0.4 mol•dm−3 solution in DMSO are hydrogen bonded to at least one D2O at a D2O concentration of 0.3 mol•dm−3. It is also clear that each of the C=O groups is multiply hydrogen bonded at relatively low aqueous concentrations and that the basicities of the two C=O groups are unequal. In addition to providing calculated infrared spectra, which guided the analyses of the infrared data, the computational chemistry provides energetic data for the different hydrogen bonded species. These support the conclusion that the C=O basicities differ markedly; moreover, these calculations strongly point to significant cooperativity in the hydrogen bonding. Thus, formation of additional hydrogen bonds at C=O significantly strengthens hydrogen bonds formed at the N−H groups.

Hydrolysis Aqueous Sulfuric Acid of Poly(e-caprolactam) at High pH and at Moderately pH

MANTECA-DIEGO, Consolacion (Universidad Politécnica de Madrid) DOMENECH, Sandra (Universidad Politecnica de Madrid)

The rate of hydrolysis of poly(e-caprolactam), in aqueous sulfuric acid as solvent and catalyst was studied at 343.2 K over the sulfuric acid concentration range of 4.0 to 14.0 M by considering as a measure of the hydrolysis the flow time measured by this viscometric technique. Hydrolysis rates were measured by two independent viscometer of 0.36 and 0.58 mm f (capillary bore). Viscosity data have been analyzed by means of the relation between the macroscopic viscosity h and molecular weight M or number of hydrolyzable amide links (- NHCO-) considering that our macromolecule behaves either as a gaussian hydrodynamically permeable coil. The experimental results satisfy, even for high degrees of conversion, a first-order rate equation. Kinetic linear free energy linear relationships (LFERs) and Ho (Hammett acidity function), HA (amide acidity function) and aH2O (water activity coefficient) functions are discussed.

Estimation of the "hydrophobic reactivity" of SDS by the use of BPh4- anions

BOUGHAMMOURA Sondès, M'HALLA Jalel
Faculty of Sciences, UR « Electrolytes », University of Monastir, 5000 Monastir, Tunisia.

Self-association of ionic amphiphiles into micelles is governed by the intricate balance between "hydrophobic interactions" among the nonpolar side chains and "electrostatic-hydrophilic" interactions between the ionic head groups with themselves, counterions and water. Sodium dodecylsulfate is "the prototype" for the investigation of anionic surfactants. However, despite considerable efforts, our understanding of the structural and transport properties of SDS, is far from complete. Indeed, the data reported for this surfactant on its both structural and apparent charge numbers $\mathbf{Z_S}$, $\mathbf{Z_{ap}}$, or on its degree of counterion dissociation α, or on its mobility, scatter markedly. These differences are not solely a consequence of the specificities of the employed techniques, but they result especially from the differences between the models adopted in order to interpret the data of a one given technique. In this work, electric conductivity data of SDS are analyzed in terms of the mass-action model in combination with a generalized Fuoss's association approach and the Onsager-Kim-MSA conductivity theory, by treating the aqueous monomers, micelles and counterions respectively of total concentrations: $\mathbf{C_M}$, $\mathbf{C_P}$ and $\mathbf{C_I}$, as a solution of mixed electrolytes at 25°C.

Much attention is given to analyzing the conductivity of this micellar system when hydrophobic anions BPh_4^- of total concentration $\mathbf{C_X}$, are added to sodium dodecylsulfate SDS. The displacement of BPh_4^- ions from bulk water into the organic microphase of the micelles can occur depending essentially on the relative competition between the strength of the hydrophobic hydration of BPh_4^- ions and their affinity for the nonpolar side chains inside SDS. Conductivity data have therefore been employed to evidence and to estimate the "hydrophobic chemical reactivity" of SDS toward negative organic species. Quantitatively this "surfactant efficiency" is defined by the number « **n** » of BPh_4^- ions absorbed by **one** SDS micelle. Determination of « **n** » is obtained by adjusting the theoretical specific conductance χ_{th} to its corresponding experimental value χ_{exp} according to the following system of equations involving the variables $\mathbf{Z_{ap}}$, α, β, γ, « **n** » and the ionic conductivities λ_p, λ_M, λ_I and λ_X:

$\chi_{th} = 10^{-3}\sum_i \nu_i C_i \, |Z_i| \, \lambda_i$; with: (i : I ≡ Na^+, M ≡ SD^-, X ≡ BPh_4^-, P ≡ micelle) and: $\nu_I \equiv \alpha$, $\nu_M \equiv \beta$, $\nu_X \equiv \gamma$.

$$\lambda_p = \{(eF\alpha)\,|Z_s|\,(6\pi\eta R)^{-1} + \Delta\lambda_p^{el}\}(1+\beta_P^{ir})^{-1}(1+[(2/3)(Z_s\alpha)^2(R_w/R)^3]L_b(1-\varepsilon_{.}/\varepsilon)[R^{-1}-d^{-1}])^{-1}$$

$$\lambda_I = \{50.1 + \Delta\lambda_I^{el}\}(1+\beta_I^{ir})^{-1} \;;\quad \lambda_M = \{22.9 + \Delta\lambda_M^{el}\}(1+\beta_M^{ir})^{-1} \;;\quad \lambda_X = \{19.4 + \Delta\lambda_X^{el}\}(1+\beta_X^{ir})^{-1}$$

$\mathbf{Z_{ap}} = -|Z_s|(\alpha - \beta)/(1 - \beta) - \mathbf{n}(\alpha - \gamma)/(1 - \gamma)$; $\gamma = 1 - \mathbf{n}|Z_s|^{-1}(1 - \beta)(C_M/C_X)$; $(1 - \beta)/(\beta) = K_M|Z_s|(\beta C_M)^{(|Z_s|-1)}$
$[(1 - \alpha)/(\alpha C_P)] \cong (4\pi R^3/3)\exp\{b'(\mathbf{Z_{ap}}/Z_s)(1 - Rd^{-1})\}$; $C_P = (1 - \beta)C_M/|Z_s|$; $d = R + 1/2\Gamma$; $b' = |Z_s|L_B/R$
$\mathbf{Z_S} = -54$, $K_M \cong 10^{104}$ is the micellization constant, L_B is the Bjerrum length, $F = N_A e$, is the Faraday, R is the micelle radius and Γ is the Debye-MSA screen parameter. R_w, η, ε are respectively the molecular radius, the viscosity and the static permittivity of water, and ε_{∞} is the permittivity at infinite frequency. The different $\Delta\lambda_i^{el}$ and β_i^{ir} corrections express respectively the electrophoretic and the ionic relaxation effects according to the Onsager-Kim-MSA theory. We also take into account both hydrodynamic and dielectric friction effects on the micelles.
Calculations and comparison with the experimental data show that at 25°C, and in the range of counterions concentration $\mathbf{C_I}$ between 0.015M to 0.03M, the mean value of the "SDS efficiency" is about **n** = 0.5.
The compatibility between the MSA theory and the "cell model" is also discussed via the Γ parameter.

An Infrared and Computational Study of Hydrogen Bonding to Uracil

HAJIMOHAMMADPOOR, Maryam (University College Dublin) WAGHORNE, Earle (University College Dublin)

Uracil, one of the nucleic acid pyrimidine bases is present in RNA but not in DNA, where it is replaced by thymine. The principle role of the nucleic acid bases is to provide reversible anchorages, through hydrogen bonding and so exploring these interactions is important in understanding these systems. Preliminary studies of a number of pyrimidine bases and related compounds showed that they are remarkably strong hydrogen acceptors.
Infrared spectroscopy has been used to elucidate the hydrogen bonding to a number of chromophores in aprotic + protic mixed solvents; the technique allows both the numbers of hydrogen bonds formed and the relative populations of differently hydrogen bonded species to be determined. In the case of uracil the analysis is complicated by the presence of the two C=O moieties, both of which contribute to the infrared spectra and both of which may form multiple hydrogen bonds. Thus the infrared measurements were augmented by computational calculations (Density Functional method with B3LYP and the 6-31+G (p,d) basis set) of uracil hydrogen bonded to DMSO through the two N−H protons and up to three water molecules on each of the C=O groups. The results confirm that uracil, in DMSO, is a remarkably strong hydrogen bond acceptor; thus, for example, essentially all of the uracil molecules in a 0.4 mol•dm−3 solution in DMSO are hydrogen bonded to at least one D2O at a D2O concentration of 0.3 mol•dm−3. It is also clear that each of the C=O groups is multiply hydrogen bonded at relatively low aqueous concentrations and that the basicities of the two C=O groups are unequal. In addition to providing calculated infrared spectra, which guided the analyses of the infrared data, the computational chemistry provides energetic data for the different hydrogen bonded species. These support the conclusion that the C=O basicities differ markedly; moreover, these calculations strongly point to

significant cooperativity in the hydrogen bonding. Thus, formation of additional hydrogen bonds at C=O significantly strengthens hydrogen bonds formed at the N–H groups.

Structure and dynamics of CO2, H2CO3, HCO3-, CO3(2-) in aqueous solutions: Ab initio molecular dynamics simulations

KALINICHEV, Andrey (Ecole des Mines de Nantes) ; KUMAR, P. Padma (Department of Physics, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, INDIA) ; KIRKPATRICK, R. James (College of Natural Sciences, Michigan State University, East Lansing, MI 48824, USA)

Aqueous carbonate species play many important roles in the global carbon cycle of our planet. Molecular scale understanding of their behavior is also crucial for the development of viable carbon sequestration technologies. Hydration structure and hydrogen bonding environments of these species strongly affect their dynamical behavior and chemical reactivity. We performed a series of detailed Car-Parrinello molecular dynamics simulations in order to clarify the molecular level picture of the structure and dynamics of aqueous carbonate species: CO2, H2CO3, HCO3-, CO3(2-). The strengths and lifetimes of H-bonds involving the carbonate species positively correlate with their total negative charge. The H-bonds donated by the C–O–H sites of the carbonate species to the neighboring water molecules are generally stronger and longer lived than those accepted by these sites from H2O. H-bond donation from H2O to CO2 is weak, but the presence of CO2 leads to noticeably stronger H-bonds and slower relaxation rates for the H-bonding network of the surrounding solvent water molecules.

The structure of electrolyte solutions and dynamics of ions near single wall carbon nanotubes

KOLKER, Arkady (Institute of Solution Chemistry of the RAS) ; GORBACHEV, Evgeny (Institute of Solution Chemistry of the RAS) ; KISELEV, Michael (Institute of Solution Chemistry of the RAS) ; FOMINA, Nadezhda (Ivanovo State University of Chemistry and Technology)

Carbon nanotubes (CN) have a series of unique properties due peculiarities their electronic properties. These electronic properties in turn are sensitive to local surroundings. Properties of CN change as in presence of gases, free radicals and ions as well. An influence of compounds located in nearest arrangement of CN depends on their nature and chirality of carbon nanotubes. Despite of many theoretical and experimental works in this field, the influence of functional groups and chirality of nanotubes is not enough studied. This is the main aim of this work. In this work , CN with different chirality (6,0), (6,4), (6,5), (7,0), (7,5), (10,0), (13,0) in aqueous

electrolyte solutions have been studied by MD simulation. The simulation was carried out using standard procedure with program package "GROMACS 4.0.4" in NVT ensemble at temperature of 300 K. The local density distribution in axial and radial directions has been calculated for analysis of atomic density near nanotubes for functionalized by hydrophilic groups CN. The local density as function of polarity in direction of nanotube axis at distances of 0,25 (CN–H), 0,41 (CN–OH) и 0,61 нм (CN–COOH) decreases. The nanotube in liquid systems has an effect on structural and dynamical solvent properties. The first peak on RDF(O-H) decreases, but the second one increases in comparison with net solvent. The average number of hydrogen bonds per one oxygen atom for all considered systems is 1.77 and average coordination number is 4.06, what is lower than in liquid water. The change in self-diffusion coefficient of ions and water molecules depending on the distance from the axis of the nanotube will be discussed in the report. The extremum of this dependence for all systems observed in layer 2, which corresponds to a distance of 0.66-0.86 nm from the nanotube axis. The gradual increase in the mobility of the particles has been observed from second up to sixth layer inclusive.

This work has been supported by RFBR No. 11-03-00586-a, 11-03-00122-a

Complexes of sulfuric acid with N,N-dimethylformamide: an ab initio investigation

SAFONOVA, Liubov (Institute of Solution Chemistry of the RAS); KISELEV, Michael (Institute of Solution Chemistry of the RAS) ; FEDOROVA, Irina (Ivanovo State University of Chemistry and Technology)

Nowadays, particular attention is focused on investigation of polymer electrolyte membrane fuel c
Thus, the complex formation of sulfuric acid in gas phase is considerable interest with regard to elucidating
details of acid–base interaction and studying proton transfer mechanism.

At present report the formation of $(H_2SO_4)_2$, H_2SO_4–DMF and $(H_2SO_4)_2$–DMF hydrogen bon
complexes was investigated by means of *ab initio* and DFT calculations. All calculations were performed
the Gaussian-03 program. Since there are no experimental data for sulfuric acid complexes, we have tested
accuracy of our calculations on a single H_2SO_4 molecule because of the experimental geometries
thermodynamic data are available. The calculated geometric parameters of molecule derived from
B3LYP/cc-pVQZ are in excellent agreement with experimental data determined from microwave spectr
gaseous H_2SO_4 molecules. Therefore, the $(H_2SO_4)_2$, H_2SO_4 –DMF and $(H_2SO_4)_2$–DMF hydrogen bon
complexes are expected to be described better at the B3LYP/cc-pVQZ level of theory.

There are three configurations of $(H_2SO_4)_2$, two of them have almost identical energies but very diffe
structure. The lowest energy has dimeric complex in which O–H parts of the one acid molecule are linked
O(=S) atoms of the other acid. The equivalent O...O distances are 3.21 E, indicating a weak hydrogen bo
The hydrogen bonds energy for this configuration is only the -41.41 kJ/mol. The second structure of $(H_2SO$
complex has also two symmetric hydrogen bonds but between the O–H part and O(=S) atom of the one
and the same parts of other molecule. The O...O distances are 2.66 E and bond angles correspond to175
The values obtained of geometrical parameters allow to suppose the formation of rather strong hydrogen bo

in $(H_2SO_4)_2$. The bond energy of such complex is equal to -65.66 kJ/mol. The formation energy of
complex with three hydrogen bonds (ДE=-61.48 kJ/mol) are close to energy value of previous comple
hydrogen bonds in the acid dimer are not equivalent. The one strong hydrogen bond (r(O...O)=2.66 E)
weak (O...O distances are 2.85 E and 2.86 E) exit between the acid molecules. The H–O...H an
distorted from 180°, being 159.0°, 165.4° and 165.9°. For reasons given we are considered the only mo
dimeric acid complexes with H_2SO_4 or $(H_2SO_4)_2$ proton and *DMF* oxygen are more strong than acid
The covalent O–H bond of the sulfuric acid elongates by 0.06 E relative to that in free H_2SO_4 for H
DMF and by 0.07-0.11 E for $(H_2SO_4)_2 - DMF$ complexes whereas one stretches by 0.02-0.03 E for $(H$
The O...O distance is 2.56 E for $H_2SO_4 - DMF$ and 2.46-2.52 E for $(H_2SO_4)_2 - DMF$ complexes.
bond angles in both complexes are close to 180°. The results of the NBO analysis have shown the
transfer value at H-bond formation and the stabilization energy of interacting orbitals are significantl
for complex with dimeric sulfuric acid than for $H_2SO_4 - DMF$.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 11-03-00311)

Physico-chemical properties of proton conducting electrolytes at confined geometry of polymeric gel

SHMUKLER, Liudmila (Institute of Solution Chemistry) ; NGUEN VAN, Thuc (Ivanovo State University of Chemistry and Technology) ; SAFONOVA, Liubov (Institute of Solution Chemistry)

Polymer electrolytes are preferred in comparison with liquid ones because of greater opportunities for their applications. The conductivity of gel electrolytes is significantly higher, about 1 mS cm-1 at ambient temperature, of solid polymer electrolytes that is ample to apply its in portable electronic equipment. Together with high proton conductivity in a wide range of fluctuations in humidity and temperature of environment, they should have high chemical and thermal stability and elasticity as well. All of the above requirements can be achieved by optimum combination of gel components, namely, the polymer matrix, plasticizer, and a donor of protons. The aim of this study was to investigate the physico-chemical properties of proton-conducting gel electrolytes based on poly(methyl methacrylate) (PMMA), doped with inorganic solutions (phosphoric acid, sulfuric acid) and organic (benzoic acid, salicylic) acids in the N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAA) and propylene carbonate (PC).The ionic conductivity of the gels in the temperature range 25 - 65oC has been measured by method of electrochemical impedance spectroscopy. We found that gels of ~ 9 wt.% PMMA - [0.1M acid - DMF] the electrical conductivity decreases in the series of acids: sulfuric > salicylic > phosphoric > benzoic, which correlates with the dissociation constants of acids. The electrical conductivity of gels prepared with different solvents decreases in accordance with the following series DMF > DMAA > PC, which may be due to the influence of viscosity. The viscosity and the influence of acid concentration and the polymer, as well as the molecular weight of PMMA on the conductivity have been obtained for gel electrolytes based on solutions of inorganic acids. Electrical conductivity of the obtained gels higher the conductivity of acid solutions used for their preparation. This is probably due to the fact that the polymer matrix can both promote the dissociation of acid and take part in proton transfer in accordance with Grotthuss mechanism of proton transport. The calculated values of activation energy lower the activation energy of viscous flow that indicates a significant contribution of Grotthuss mechanism in the process of proton transport in gel electrolytes. The addition of water to the gel electrolyte increases the conductivity due to increased degree of acid dissociation, but the content of H2O for more than 7 wt.% lead to destruction of gel. The obtained gel electrolytes are thermally stable up to temperatures ~ 90oC as follow from TGA and DSC methods.

This work was financially supported by Russian Foundation for Basic Researches (grant 11-03-00311-a).

Description of aqueous solutions of ammonium and bulky anions within the BiMSA model: Towards the description of ionic liquids in water

PAPAICONOMOU, Nicolas (Université de Savoie - LCME) ; SIMONIN, Jean-pierre (PECSA - CNRS - Université Paris VI) ; BERNARD, Olivier (PECSA - CNRS - Université Paris VI)

With the aim of better understanding the behavior of ionic liquids in water, the BiMSA model was first used to describe aqueous solutions containing polyalkylammonium cations or bulky anions such as sulfate, methylsulfate, trifluoroacetate and trifluoromethanesulfonate. The model accurately described the osmotic coefficients of the solutions, with physically sound parameters. Values obtained for the ion diameters (cation or anion) were found to be in good agreement with literature values. Values for the association constants also appeared to consistently increase with the size of anion and cation. The concentration dependent diameter for the cation diameter used within the BiMSA model is generally related to the solvation sphere surrounding simple cations. In the present case, this parameter appeared to account for another phenomenon: the flexibility of alkyl chains appended to an ammonium cation. In order to apply this model to aqueous solutions of ionic liquids, a preliminary study of the experimental data set was first carried out. The significant discrepancy found between data limited the thermodynamic modelling of such data.

Comparative studies of hydration of some oxoanions

EKLUND, Lars (SLU) ; HOFER, Thoas (University of Innsbruck) ; PERSSON, Ingmar (SLU) ; RODE, Bernd (University of Innsbruck)

The interaction between solvent and solute is a very important chemical property that has large impact on the chemical reactions taking place. The structures of hydrated sulfite, sulfate, selenite and selenate ions in aqueous solutions have been determined by large angle X-ray scattering (LAXS), and by theoretical simulations. The hydration shell of the sulfite and selenite ions have been shown to be asymmetric, seen as two different central ion-water distances, and in the case of sulfite ion the same observation is made in the angular radial distribution (ARD) function from the theoretical simulation. This asymmetric structure may have large influences on the physico-chemical properties as water change rate and mechanism. The water exchange is relatively fast and has the same mechanism on all oxygens in the sulfate ion, while the water exchange rate is much slower on the oxygens in the
sulfite ion, and instead in principle all water exchange take place in close vicinity of the lone electron pair. These divalent anions are all weak structure makers in aqueous solution which affects their thermodynamic properties. These physico-chemical properties help us to understand the chemistry of these ions in aqueous solution.

The interaction of iron and oxygen on oak wood – determination of degree of deterioration of iron impregnated fresh oak wood by tensile strength and chemical analyses and comparison with Vasa wood

JOHANSSON, Charles (SLU) ALMKVIST, Gunnar (SLU) ; BJURHAGER, Ingela (KTH)

Wood degradation in the warship Vasa has been studied systematically regarding the chemical and physical properties as function of time. It is still a question whether the deterioration reactions still go on or if they did stop soon after the ship was salvaged. Several series of fresh oak wood samples was stored in aqueous solutions containing iron(II) chloride. The force required to pull the sample apart was determined. Variation of time and concentration of oxygen exposure showed that the deterioration of the wood takes place at the initial stages. Water extracts of ground samples indicated an increase in the production of low-molecular organic acids in the wood tissue and a decrease to pH~2 was observed. The presence of iron compounds throughout the Vasa wood is certainly an important factor to the deterioration reactions and in the wood causing decreased mechanical strength. However, these reactions are also dependent on several other parameters such as temperature, humidity, diffusion rate of oxygen and transport properties of water in the wood. It is believed that as soon as the Vasa was exposed to air these deterioration reactions started, and it is possible that these processes still goes on deep into the timbers.

Solution Properties and Cross-linking Reaction of Syndiotactic-like PVA Solution

OH, Tae Hwan (Yeungnam University) ; SEO, Young Ho (Yeungnam University) ; HAN, Sung Soo (Yeungnam University) ; LYOO, Won Seok (Yeungnam University) ; CHO, Hye Won (Yeungnam University)

Syndiotactic-like poly(vinyl alcohol) (PVA) was polymerized with suspension polymerization. PVA solution was prepared to make embolization coil via gel spinning. Rheological properties of PVA solution were investigated and the optimum concentration of PVA solution was determined. The optimum concentration of PVA solution was 13 wt%. The PVA solution extruded into coagulation bath, which is composed of water and methanol mixture. As-spun PVA fibers were drawn to its maximum draw ratio. Molecular orientation and crystallinity increased with increasing draw ratio. The crystallinity changed from 53 to 74% with increasing draw ratio. The draw PVA fibers were used to make embolization coils. The PVA fibers were coiled on glass rod and annealed with various temperature and times. Annealing of 30 minutes at 140C was required to retain the coil shape. Tenacity of the coil increased with increasing annealing time and temperature up to 1.7 times higher than the control.

NMR Relaxation Studies on 1-Alkyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)amide

KANAKUBO, Mitsuhiro (AIST) HARRIS, Kenneth R. (The University of New South Wales @ Australian Defence Academy) ; TSUDUKI, Seiji (AIST) ; UMECKY, Tatsuya (AIST) ; MAKINO, Takashi (AIST) ; SUZUKI, Akira (AIST)

Ionic liquids (ILs) have recently attracted much attention as novel media in a variety of fields. The density, viscosity, electrical conductivity, and ionic diffusion coefficients in ILs are necessary properties for understanding their fundamental nature. We have precisely determined such macroscopic properties for a series of imidazolium-based ILs over wide ranges of temperature and pressure [1-2]. The transport properties were discussed in terms of the velocity cross-correlations, the Nernst-Einstein equation, and the fractional form of the Stokes-Einstein relation. In the present work, 1H, 19F, and 13C NMR relaxation times and the 13C nuclear Overhauser enhancement factors for a series of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide salts, [CnMIM][Tf2N] with n = 2, 4, 6, and 8 have been measured over a wide range of temperature at atmospheric pressure. The molecular ion dynamics in the ILs is discussed in terms of the reorientational motions of CH vectors at different chemical positions in relation to the ionic translational diffusion coefficients and the macroscopic viscosity. The experimental results are also compared with those of the molecular dynamics simulations.

[1] K. R. Harris, M. Kanakubo, N. Tsuchihashi, K. Ibuki, and M. Ueno, J. Phys. Chem. B, 112, 9830 (2008). [2] M. Kanakubo, K. R. Harris, N. Tsuchihashi, K. Ibuki, and M. Ueno, J. Phys. Chem. B, 111, 2062 (2007).

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

Physicochemical Properties of Diglyme-Lithium Bis(trifluoromethanesulfonyl)amide Solutions

KANAKUBO, Mitsuhiro (AIST) ; SONNLEITNER, Thomas (University of Regensburg) ; BUCHNER, Richard (University of Regensburg) ; KODAMA, Daisuke (Nihon University) ; MAKINO, Takashi (AIST) ; UMECKY, Tatsuya (AIST) ; SUZUKI, Akira (AIST)

Equimolar mixtures of diglyme (i.e. diethylene glycol dimethyl ether) and lithium salts show unique physico-chemical behavior resembling ionic liquids. This arises from the ability of diglyme to act as a bidentate ligand for the lithium cation. In the present paper, we investigate electrolyte solutions composed of diglyme and lithium bis(trifluoromethanesulfonyl)amide (LiTf2N) to discuss intermolecular interactions in such systems. Densities, r, viscosities, h, and electrical conductivities, k, were determined at various temperatures as a function of salt concentration up to ~30 wt-%. The partial molar volume and the viscosity B coefficient of the salt were derived from the concentration dependence of r and h, respectively. Molar conductivities, L = k/c, and viscosities were analyzed in terms of the empirical Walden relation. Furthermore, broadband dielectric spectra in the microwave range are presented.

This work was partially supported by the JSPS Institutional Program for Young Researcher Overseas Visits.

Absorption and Desorption Properties of CO2 in DBU-Alcohol Systems

KANAKUBO, Mitsuhiro (AIST) ; MAKINO, Takashi (AIST) ; SUZUKI, Akira (AIST) ; TAKAMUKU, Toshiyuki (Saga University)

DBU-alcohol solutions can reversibly absorb CO2 gas under an ambient condition [1], where DBU is 1,8-diazabicyclo[5.4.0]-undec-7-en. The DBU-alcohol systems are important as CO2-chemsorbing materials; however, no systematic investigation has been made. As our first study on the DBU-alcohol solutions, the amounts of CO2 absorption at 25°C and desorption as a function of temperatures (25 → 60 → 80 → 100 → 120°C) have been examined in a variety of alcohols. The properties of DBU-alcohol systems were compared with those of a common monoethanolamine(MEA)-water system. The capacity of CO2 absorption in DBU-alcohol systems is much larger than that in MEA- water, however it is almost independent of a kind of alcohols. It is revealed that a DBU molecule stoichiometrically reacts with a CO2 molecule in every alcohol. On the other hand, DBU-alcohols can desorb much larger amounts of CO2 at lower temperatures than MEA-water, which can reduce the thermal energy in the recovery of CO2. Moreover, the desorption process is strongly dependent on the alcohols. This interesting desorption behavior could be attributed to hydrogen bonding interactions in DBU-alcohols. In the presentation, we will discuss the CO2 absorption and desorption mechanisms in DBU-alcohols in terms of solution structures. 1. (a) Camper, D.; Bara, J. E.; Gin, D. L.; Noble, R. D. Ind. Eng. Chem. Res. 2008, 47, 8496. (b) Heldebrant, D. J.; Yonker, C. R.; Jessop, P. G.; Phan, L. Energy Environ. Sci. 2008, 1, 487. (c) Heldebrant, D. J.; Yonker, C. R.; Jessop, P. G.; Phan, L. Energy Procedia 2009, 1, 1187.

UMECKY, Tatsuya (Saga University)

Raman spectroscopic study on N-methylimidazolium based Protic Ionic Liquids

UMEBAYASHI, Yasuhiro (Kyushu University) ; DOI, Hiroyuki (Kyushu University) ; SONG, Xuedan (Kyushu University) ; KANZAKI, Ryo (Kagoshima University)

Protic Ionic Liquids (PILs) with a dissociable hydrogen atom have been attracted remarkable attention as solvents for water insoluble proteins, acid catalytic reactions and electrolytes of fuel cells. Acid-base property of solvent PILs strongly affects in such applications. Autoprotolysis constant (K¬S) is one of measures of the solvent acid-base property. We reported thermodynamics of autoprotolysis reaction in ethylammonium nitrate (EAN) based on the direct pH measurement using appropriate electrodes. Recently, pKs for N-methylimidazolium [C1Im+] based PILs were also determined with varying anion species, which suggests that, due to the large pKs values, the ionic species are predominant in PILs combined with bis-(trifluoromethanesulfonyl)amide (TFSA), trifluoromethanesulfonate (TFS) and trifluoroacetate (TFA) anions. On the other hand, pKs values for [C1Im+][HCOO–] and [C1Im+][CH3COO–] were practically negative, indicating that neutral species of N-methylimidazole and corresponding acids are mainly exists in these liquids. In this contribution, Raman spectra were measured to clarify the predominant species in above 5 PILs composing of N-methylimidazolium. Among them, Raman spectra for [C1Im+][TFSA–], [C1Im+][TFS–] and [C1Im+][TFA–] ionic liquids were well explained with predicted Raman spectra by DFT calculations, so that Raman spectroscopic study strongly supports the potentiometric investigation. Similarly, all of observed Raman bands for [C1Im+][HCOO–] and [C1Im+][CH3COO–] were reasonably ascribed to those predicted for N-methylimidazole and corresponding acids. Thus, it was confirmed that neutral species are predominant, in other words, ionic species are practically negligible. These spectroscopic facts suggest that the latter 2 liquids are pseudo ionic liquid rather than ionic liquids. Nevertheless, it is worth mentioning that these pseudo ionic liquids have considerable ionic conductivity. In this context, pseudo ionic liquids could be a candidate for an entirely new solvent class. We discuss possible ion conductive mechanism in these pseudo ionic liquids.

Determination of Distance-dependent Viscosity of Mixtures in Parallel Slabs using Non-equilibrium Molecular Dynamics

PAřEZ, Stanislav (Institute of Chemical Process Fundamentals of the ASCR, Prague) ; PřEDOTA, Milan (Faculty of Science, University of South Bohemia, Ceske Budejovice)

In the last years we have been studying by molecular dynamics the dynamic and structural properties of aqueous solutions in contact with metal-oxide surfaces, mainly rutile [1,2]. We present a technique for determination of shear viscosity of mixtures in planar slabs from non-equilibrium computer simulations by applying external force parallel with the surface. Distance-dependent viscosity of the mixture, given as a function of the distance from the surface, is determined from analysis of the resulting velocity profiles of all species subject to resulting Poiseuille flow. Our investigation extends the commonly explored viscosity of pure fluids by the calculation of the viscosity of mixtures. As a benchmark, we present results [3] for highly non-ideal water + methanol mixture in the whole concentration range. It will be shown that dynamical properties of a liquid flowing in channels or pores of width of few nanometers cannot be automatically presumed to adopt experimental values measured in bulk phase.

[1] M. Předota, Z. Zhang, P. Fenter, D. J. Wesolowski, and P. T. Cummings (2004), J. Phys. Chem. B 108, 12061-12072. [2] M. Předota, P. T. Cummings, and D. J. Wesolowski (2007), J. Phys. Chem. C 111, 3071-3079.[3] S. Pařez and M. Předota: Determination of Distance-dependent Viscosity of Mixtures in Parallel Slabs using Non-equilibrium Molecular Dynamics, to be submitted to PCCP.

Molecular simulations of electrokinetic phenomena at the solid-liquid interface

PAřEZ, Stanislav (Institute of Chemical Process Fundamentals of the ASCR, Prague) ; PřEDOTA, Milan (Faculty of Science, University of South Bohemia, Ceske Budejovice) ; MACHESKY, M. L. (University of Illinois, Champaign)

In the last 10 years we have been studying by molecular dynamics (MD) the structural and dynamic properties of aqueous solutions in contact with metal-oxide surfaces, mainly rutile [1-4]. We will present the results of our equilibrium and non- equilibrium MD simulations focusing on the molecular level origin of electrokinetic phenomena - electroosmosis and electrophoresis. We will comment on the asymmetry of the density profiles of cations and anions at positive and negative surfaces, discuss the properties of the diffuse and shear layers, if definable at all on the molecular scale, and present our zeta potential predictions from molecular simulations. Our results of zeta potential are in qualitative agreement with experimental data [5]. However, our molecular explanation is rather contradictory to at least some of the commonly used theories of the solid-liquid interface including the common double- or triple- layer models. We observe that the composition and structure at the interface, influenced by the surface charge, are the key factors, while the electrostatics of the aqueous solution is rather independent of the surface charge. This debate is an important step in validating/challenging the theories of the solid- liquid interface and making as close link as possible between molecular simulations and experiments, which will ultimately lead to a deeper understanding of the solid- liquid interface.

[1] M. Předota, A. V. Bandura, P. T. Cummings, J. D. Kubicki, D. J. Wesolowski, A. A. Chialvo, and M. L. Machesky (2004), J. Phys. Chem. B 108, 12049-12060. [2] M. Předota, Z. Zhang, P. Fenter, D. J. Wesolowski, and P. T. Cummings (2004), J. Phys. Chem. B 108, 12061-12072. [3] M. Předota, P. T. Cummings, and D. J. Wesolowski (2007), J. Phys. Chem. C 111, 3071-3079. [4] M. L. Machesky et al. (2008), Langmuir 24, 12331-12339. [5] M. V. Fedkin, X. Y. Zhou, J. D. Kubicki, A. V. Bandura, S. N. Lvov (2003), Langmuir 19, 3797-3804.

Experimental study and thermodynamic analysis of quaternary reacting systems with ester synthesis reaction in solution

TOIKKA, Maria (Saint-Petersburg State University) ; TROFIMOVA, Maya (Saint-Petersburg State University) ; TSVETOV, Nikita (Saint-Petersburg State University) ; TOIKKA, Alexander (Saint-Petersburg State University)

Phase and chemical equilibria in two quaternary reacting systems with ester synthesis reaction in solution has been experimentally studied and modeled. Because of limited solubility of ester and water the miscibility gap in solution is a common occurrence for such systems. Accordingly the objects of our study were liquid – liquid phase transitions, chemical reaction (esterification) and coupled processes.

Phase transitions accompanied by chemical reaction are one of the main types of coupled processes and are of great importance as effective and energy-saving industrial processes. The research of such coupled processes is a complex problem and requires new experimental data sets on phase equilibrium (PE), chemical equilibrium (CE), simultaneous PE and CE and on the run of nonequilibrium chemical reaction in homogeneous and heterogeneous areas. In spite of practical significance of coupled processes for chemical engineering and basic thermodynamic theory of solution the database on reacting systems with miscibility gap in solution is rather limited. Our work presents a new experimental study of solubility, chemical equilibrium and critical phenomena in acetic acid – ethanol – ethyl acetate – water and acetic acid – n-propanol – n-propyl acetate – water systems at various temperatures (293.15 K, 303.15 K and 313.15 K). The solubility and critical phenomena were studied by cloud-point techniques method. The liquid-liquid equilibrium (LLE) and CE were investigated in laboratory set-up with the use of gas chromatographic (GC) analysis. CE had been determined for more then 200 quaternary mixtures (for each quaternary system). The new experimental data sets on the run of solubility curve were obtained for four ternary sub-systems with limited miscibility (acetic acid – ethyl acetate – water and ethanol – ethyl acetate – water, acetic acid – n-propyl acetate – water and n-propanol – n-propyl acetate – water systems). The compositions and dispositions of critical points in sub-systems were also determined at 293.15 K, 303.15 K and 313.15 K. The same experiments were carried out for both quaternary systems acetic acid – ethanol – ethyl acetate – water and acetic acid – n-propanol – n-propyl acetate – water. The disposition of tie-lines in composition tetrahedron was determine with the use of GC analysis. On the base of experimental data sets the binodal surfaces and the surfaces of CE in the composition tetrahedron were constructed. For acetic acid – n-propanol – n-propyl acetate – water system at 313.15 K we used our previous experimental data set [1]. The special task of the work was the experimental determination of critical states of LLE in quaternary systems including the case of CE. The critical states of LLE in quaternary systems belong to the curve in composition tetrahedron (critical curve). The points of intersection of critical curve and CE surface correspond to the critical points of LLE in CE state. The disposition of these points has been determined for the system with propyl acetate synthesis reaction at 293.15 K, 303.15 K and 313.15 K. For both systems (with ethyl acetate and propyl acetate synthesis reaction) the experimental data sets reflect the transformation of mutual disposition of the solubility surfaces and CE surfaces with temperature changes. Accordingly these data represent the temperature shifts of the critical curves. Thermodynamic models (NRTL and UNIFAC) were used for the modeling of LLE in systems investigated. The main aim of this part of the work was the application of UNIFAC method for approximation of LLE. The calculated data sets are in satisfactory agreement with experimental data. Acknowledgment This study was supported by Russian Foundation for Basic Research (grant RFBR 09-03-00812-a). Authors also acknowledge Saint-Petersburg State University for the research grant (reg. No 12.0.105.2010) and financial support (reg. No 12.41.417.2011). References 1. M.A. Toikka, B.I. Gorovits, A.M. Toikka. Rus. J. Appl. Chem., 81, 223 (2008).

Study of destruction of water structure in the binary mixtures N,N-dimethylformamid-water and tetrahydrofuran-water

MIRZAEV, S.z. (Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, Tashkent 100135, Uzbekistan) ; EGAMBERDIEV, K.b. (Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, 100135 Tashkent, Uzbekistan) ; ZAITDINOV, M.r. (Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, 100135 Tashkent, Uzbekistan)

Sound attenuations of aqueous mixtures of dimethylformamid (DMFA) and tetrahydrofuran (THF) have been measured in the entire concentration in the temperature range of 283,15-303,15 K by using pulse method. For each concentration measurements were made between 10 MHz and 100 MHz. Actually sound attenuation strongly dependence on concentration and temperature in both mixtures. For instance in DMFA-water system attenuation's bottom have been observed concentration range of 5-10 mol percent of DMFA and maxima have been observed in 20 mol percent of DMFA. With increase temperature these characters were disappear. Behaviour of sound attenuation in THF- water system just more different than DMFA-water system. Sound attenuation increased up to 20 mol percent of THF. Thereafter it was monotonically decrease, a maximum point observed at 18-20 mol percent of THF. Thus general features of the attenuation had extreme character. If non-elctrolyt molecules were added to mixture it influenced to structure of water. For DMFA-water mixtures it is related to changes in the structure of water caused by the influence of non-electrolyt molecules. This process has two consequences. Probably it causes a destruction of water structure because of accommodation of hydrophobic radicals in the mixtures and the displacement of free water molecules or it can cause a certain stabilization of the water structure. The work has been supported by Grant FA-F082 Academy of Sciences of Uzbekistan.

Study of density and adiabatic compressibility fullurene (C60) solutions

MIRZAEV, S.z. (Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, 100135 Tashkent, Uzbekistan) ; TELYAEV, S.k. (Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, 100135 Tashkent, Uzbekistan) ; AVDIEVICH, V. (Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, 100135 Tashkent, Uzbekistan)

One of most dynamically developing directions of condensed matter physics is connected with research of fullerenes and their derivatives. The originality of molecular structure of fullerenes causes their unusual behaviour in solutions. Fullerenes - the unique soluble form of carbon. They possess appreciable solubility in a wide class of organic solvents.

All-round studying of nonwater solutions of fullerenes is of great importance for the decision of some applied and fundamental problems. Existing methods of reception and division of their mixes are based on use of solvents. Because of small structural distinctions of molecules of fullerenes C60 and C70 there are relatives such properties as solubility and adsorbability. At the same time effective division of fullerenes from soot is based on distinctions in these properties at their rather high solubility in some organic solvents. Earlier some features of solutions of fullerenes in nonwater solvents have been found. So, it has been found, with a Brillouin scattering technique, that in some solvents value of ultrasonic velocity decrease linear with increase of C60 concentration.

In this work it was measured value of ultrasonic velocity, ultrasonic attenuation and density at ranges of temperature 283- 313 K and concentration 2,8-1,4 mg/ml. For measurements has been used fullerene C60, and as solvent—toluene. It was used pulse method for measurement value of ultrasonic velocity and ultrasonic attenuation. The density of solvent and solutions measured with a vibrating tube method. Results of measurements have shown that with increase in temperature value of ultrasonic velocity decrease linearly at all concentration range. Density of solutions and ultrasonic attenuation are also independent on concentration. Using values of speed and density we have calculated values of adiabatic compressibility. It has been shown that the adiabatic compressibility of fullerene solutions in toluene decreases linearly with the fullerene concentration up to the saturation limit. The work has been supported by Grant FA-F082 Academy of Sciences of Uzbekistan.

Ion pairing of biologically important ions: A global model

BONCINA, Matjaz ; BEŠTER-ROGAč, Marija

Despite the tremendous progress in understanding ion pairing which has been made over the last decades, the mechanism of ion association is not yet thoroughly known. In this regard, a method well suited for studying ion properties in different solvents is electrical conductivity.
In this work, the electrical conductivity of alkali salts of formic (formates) and acetic (acetates) acids in diluted aqueous solutions was measured as a function of temperature and salt concentration. Experimental data were analyzed by a new global model based on Quint–Viallard or\and low concentration chemical model (lcCM). It turned out, that this approach successfully describes all the measured experimental data simultaneously. Moreover, global model improves the ratio between number of fitting parameters and number of experimental points and therefore gives more reliable results. Finally, the applied global analysis of experimental data also allows the determination of the thermodynamic profile of the ion pairing process (Gibbs free energy, enthalpy, entropy, heat capacity) and transport properties of ions at the same time. Surprisingly, formates show a perceivable ion association in water which is most expressed in sodium formate[1], whereas in acetates no distinctive ion pairing in aqueous solutions can be assumed.

1. Bončina, M., Apelblat, A., Bešter-Rogač, M., J. Chem. Eng. Data, 55, 1951 – 1957, (2010)

Effect of temperature on the sorption of Selenium on alumina and montmorillonite

MOREL, Jean-pierre (Université Blaise Pascal, LMGE, UMR UBP-CNRS 6023) ; MARMIER, Nicolas (Université de Nice, LRSAE, EA 1175) ; HUREL, Charlotte (Université de Nice, LRSAE, EA 1175) ; MOREL-DESROSIERS, Nicole (Université Blaise Pascal, LMGE, UMR UBP-CNRS 6023)

Since sorption on natural or synthetic materials can attenuate the migration of the radionuclides, sorption reactions have to be taken into account in repository performance assessment models. In order to check these models at different temperatures, we performed (i) acid-base titration of alumina (ii) adsorption experiments of selenium on alumina and (iii) adsorption experiments of selenium on montmorillonite, at ambient temperature and at 40°C. Highly sensitive microcalorimeter was used to determine the heat effects accompanying the sorption of protons and selenium at the mineral-water interfaces, at ambient temperature. The enthalpic variations associated respectively to protonation and deprotonation of the alumina surface, and the enthalpic variations associated to adsorption of selenium on alumina were determined on the basis of (i) the surface sites speciation provided by a surface complexation model, and (ii) results of the microcalorimetric experiments. The protonation and deprotonation, and adsorption enthalpy values have been used to calculate the alumina surface acidity and the adsorption constants at 40°C via the van't Hoff equation. Then, the calculated curve at 40°C has been compared to the experimental alumina and montmorillonite surface titration curve and adsorption profiles of Se.

Insights on capacitive and structural properties of [BMI][PF6] confined between graphite electrodes from molecular dynamics

SALANNE, Mathieu (Université Pierre et Marie Curie) ; MERLET, Céline (Université Pierre et Marie Curie) ; ROTENBERG, Benjamin (Université Pierre et Marie Curie) ; MADDEN, Paul (University of Oxford)

Ionic liquids are studied as potential electrolytes for supercapacitors as they exhibit interesting properties such as wide electrochemical windows and high thermal stabilities. Nevertheless, some experimentally observed effects are not well understood. Simulations appear as an essential tool to explain what is seen in the experiments and to help in designing new materials with improved performances. A recently developed coarse-grained model[1], validated against experimental data for a number of bulk properties, is used to conduct molecular dynamics on the ionic liquid [BMI][PF6] confined between graphite walls. Simulations were conducted with nine potential differences, ranging between 0.0 V and 4.0 V, applied between the two electrodes.
From simulations with different applied potentials, the differential capacitances of the positive and negative electrodes can be calculated. It appears that both capacitances (C+ = 3.9 μF.cm-2 for the positive electrode and C- = 4.8 μF.cm-2 for the negative electrode) agree very well with simulation results obtained with an all- atom model[2] (C+ = 3.7 μF.cm-2 and C- = 4.6 μF.cm-2). The coarse-grained model also reproduces accurately the two-dimensional structure observed at the graphite/ionic liquid interface, namely a defective hexagonal lattice with a lattice spacing of approximately 10Å[2]. This type of two-dimensional structure was observed experimentally for [BMI][PF6] on a mica substrate[3], and in previous simulations of the interface between an inorganic molten salt and an aluminium electrode[4]. The accuracy of the simple coarse-grained model used in this study makes it a promising tool for simulations with more complex systems.
References:

[1] D. Roy and M. Maroncelli, J. Phys. Chem. B 114 (2010) 12629 [2] S. A. Kislenko, I. S. Samoylov and R. H. Amirov, Phys. Chem. Chem. Phys. 11 (2009) 5584 [3] Y. Liu, Y. Zhang, G. Wu and J. Hu, J. Am. Chem. Soc. 128 (2006) 7456 [4] M. Pounds, S. Tazi, M. Salanne and P. A. Madden, J. of Phys.: Condens. Matter 21 (2009) 424109

Acoustic, thermodynamic, and transport properties of aqueous solutions of sodium cyclamate at (298.15, 303.15, 308.15, and 313.15) K

KHARAT, Sanjeevan (Chemistry Department, H.P.T. Arts and R.Y.K. Science College, Nashik-422005, INDIA) ; MUNDE, Sachin (Chemistry Department, H.P.T. Arts and R.Y.K. Science College, Nashik-422005, INDIA)

Sodium cyclamate is intense sweetener. It is widely used in foods, beverages, and pharmaceuticals. Water plays significant role in the sweet responses. Sweeteners establish their molecular interactions with receptor through the water molecules. Therefore, understanding of the nature of sweetener-water (solute-solvent) interactions is important. Solute-solvent interactions can be studied by one of the most appropriate method which is based on temperature and concentration dependence of density, viscosity, and speed of sound data of aqueous solutions. Furthermore, density, viscosity, and refractive index of aqueous solutions of sweeteners have an important role in many fields, for example biological, pharmaceutical and food processing studies. Therefore, the experimental study of the density, speed of sound, viscosity, and refractive index properties of aqueous solutions of sodium cyclamate has been carried out at (298.15, 303.15, 308.15, and 313.15) K.

References Kharat Sanjeevan J., International Journal of Thermophysics, 2010, 31,585. Kharat Sanjeevan J., Journal of Molecular Liquids, 2008, 140, 10. Kharat Sanjeevan J., International Journal of Applied Chemistry, 2009, 4(3), 222.

Predicting the Solubility of Alkali and Alkali Earth Halides by Artificial Neural Network

TAURA, Toshiaki (University of Aichi Prefecture) Mlle. OBAYASHI, Junko (University of Aichi Prefecture)

The solubility of alkali halides (MX : M = Li, Na, K, Rb, Cs and X = F, Cl, Br, I) and alkali earth halides (MX2: M = Be, Mg, Ca, Sr, Ba and X = F, Cl, Br, I) predicted by an artificial neural network analysis is reported. By the use of ionic charges and ionic radii of cations and halide anions constituting these halides as input data, the large correlation coefficient (r2) 0.833 for predicted and experimental (from the literature) solubility in water was obtained. Furthermore, we could get higher correlations (r2 = 0.879 and 0.889) using some other physical quantities of halides in addition to ionic charges and ionic radii. On the other hand, the solubility of alkali halides in organic solvents were estimated by the use of ionic radii, the dielectric constant, the donor number (DN) and the acceptor number (AN) of solvents in which both numbers were proposed by V. Gutmann as parameters indicating electron donating and electron attracting abilities of solvents. We could obtain the highest predicted-experimental correlation for the solubility using acceptor numbers of solvents in addition to ionic radii. In this case, the most important factor to estimate solubility in organic solvents was the acceptor number (AN) of those three parameters.

Properties of Syndiotactic Poly(vinyl alcohol) Solution Containing Zirconium Oxide

OH, Tae Hwan (Yeungnam University) ; SUNG SOO, Han (Yeungnam University) ; WON SEOK, Lyoo (Yeungnam University) ; YOUNG HO, Seo (Yeungnam University) ; HYE WON, Cho (Yeungnam University)

Syndiotactic-like poly(vinyl alcohol) (PVA) was prepared with suspension polymerization and it was dissolved in a mixture of dimethylsulfoxide (DMSO) and water (8/2, v/v). Degree of polymerization was 1,700 and degree of saponification was 99.9%. Zirconium oxide ($ZrO2$), selected for radio-opacity when PVA was used in biomedical field, was mixed with the polymer solution and the content of $ZrO2$ varied with 1 to 5% by weight. The solution properties were investigated to optimize the conditions of solution spinning. Rheological properties and viscoelastic behavior of PVA solution contaning zirconium oxide were investigated. Shear viscosity was sensitive to concentration of polymer solution and an abrupt increase in viscosity was observed at 15wt%. The viscosity of the polymer decreased with increasing shear rate showing non-Newtonian flow behavior of shear thinning. Complex viscosity was measured to investigate viscoelastic properties of the solution. Variation of storage modulus and loss modulus showed gel-like behavior.

Acknowledgement This work was supported by grant No. RTI-0401-04 from the Regional Technology Innovation Program of the Ministry of Knowledge Economy (MKE).

Electrocatalytic oxidation of Acetaminophen on a Nanocamposit Ni-αAl2O3nickel modified Grafit electrode

MIRZAPOURARMAKY, Abolfazl (chercheur) OMIDVAR, Hamid (assistant prof)

Nickel electrode modified by NiOOH prepared by galvanostatic deposition was examined for their redox process and electrocatalytic activities towards the oxidation of acetaminophen in alkaline solutions. The methods of cyclic voltammetery (CV), chronoamperometry (CA) and impedance spectroscopy (EIS) were employed. The cyclic voltammogram of Ni demonstrates the formation of α/ß crystallographic forms of the nickel oxyhydroxide under prolonged repetitive potential cycling in alkaline solution. In CV studies, in the presence of acetaminophen Ni/NiOOH modified electrode shows a significantly response for acetaminophen oxidation. This work clearly shows that the Ni/NiOOH modified electrode is significant electrocatalyst for detection of acetaminophen.

Sorption of aluminium from drinking water by ion-exchangers of different chemical nature

IAKYMOVA, Tetiana (A.V.Dumansky Institute of Colloid and Water Chemistry of the National Academy of Sciences of Ukraine) ; MAMCHENKO, Oleksij (A.V.Dumansky Institute of Colloid and Water Chemistry of the National Academy of Sciences of Ukraine) ; SEMENYUK, Dmitrij (A.V.Dumansky Institute of Colloid and Water Chemistry of the National Academy of Sciences of Ukraine)

Aluminium is known as neurotoxicant and the occurrence of residual aluminium in tap water is considered as an undesirable aspect of drinking water treatment practice, when Al-based coagulants are used. The objective of the present work is to study influence of chemical nature of ion-exchange resins on efficiency of aluminium removal from drinking water. Analysis of data on aluminium forms present in water was made. Experimental study of Al sorption from tap water was carried out in dynamic mode. It is found that residual aluminium is effectively removed from drinking water with help of carboxylic cation-exchange resins due to ability of their carboxylic groups to complexation with aluminum ions. Thus it was shown that cation-exchange resin Purolite C104 removed 60 - 95% of residual aluminium from tap water. At the same time it is found that sulfonic cation-exchange resin is inefficient sorbent for aluminium removal from drinking water. Based on the obtained data as for nature of Al sorption by cationites it was offered to use anion-exchangers, which effectively adsorb humic substances for sorption of aluminium present in water. High level efficiency of water purification from aluminium by such sorbent could be achieved due to obtaining of enough high concentration of humic substances in ion-exchange resin phase in result of their sorption from water. Study on residual aluminium removal from water by strongly basic anion-exchange resin CAB 990 shown that practically the same degree of water purification is achieved as in case with carboxylic cationite Purolite C104.

The effect of anodizing parameters on morphology of TiO2 nanotube arrays

OMIDVAR, Hamid (assistant prof) GOODARZI, Saba (étudiante master)

TiO2 nanotube is a desirable nanostructure due to its photocatalytic activity and its applications in different areas. TiO2 nanotube arrays could be obtained by anodization process. morphology of this nanostructure is depend on anodization parameters such as applied voltage, type of electrolyte, temperature and time. Nanotube arrays were fabricated by anodization of commercially pure titanium in aqueous and non-aqueous electrolytes containing NH4F. The current density of anodizing was recorded by computer controlled digital multimeter. The morphology of nanotube arrays were observed by SEM and surface morphology (top-view) of nanotubes that fabricated in aqueous and non-aqueous electrolytes were compared with each other.

An analytical expression of the Ornstein-Zernike integral equation of hard-sphere liquid derived from the extended scaled particle theory

IRISA, Masayuki (Bioscience and Bioinformatics, Computer Science and Systems Engineering, Kyushu Institute of Technology, JAPAN) ; FUKUDOME, Takuya (Bioscience and Bioinformatics, Computer Science and Systems Engineering, Kyushu Institute of Technology, JAPAN)

The integral equation methods based on the Ornstein-Zernike equation have been widely used to obtain radial distribution functions, g(r), of molecular liquids. The closer which connects a direct correlation function, c(r), with a total correlation function, h(r), is necessary for solving the integral equation. However, in most cases physical meaning of the closer is ambiguous, even if the distribution functions are reproduced quantitatively. Until now, we succeeded in reproduce a radial distribution function of hard-sphere liquid in the range up to first solvatoin shell. In this work, we have obtained an analytical expression of the radial distribution function of hard-sphere liquid at all radial distances through a cavity function derived from the extended version of scaled particle theory which we have developed for non-spherical particles.

The closer in this work is derived in the same manner as the Kovalenko-Hirata closer[1] but cavity functions in the closer have the analytical expression given in XSPT. In the case of hard-sphere liquid, our new integral equation gives quantitative values of the radial distribution function. Especially, the contact value, which is a value of the first peak of the function, agrees with the Monte Carlo simulation results better than that of the PY equation. Our integral equation method in this work is expected to extend to the particles with non-spherical shapes in the next step in order to apply the method to hydration of a protein.

A. Kovalenko and F. Hirata, Chem. Phys. Lett. 349, 496 (2001)

A comparison between the morphology of chemical and electrochemical template synthesized polypyrrole nanowires

HASSANZADEH, Nafiseh (Thésard) OMIDVAR, Hamid (assistant prof)

In both chemical and electrochemical techniques, alumina membranes were used as templates for the synthesis of polypyrrole nanowires. The morphology of the synthesized polypyrrole was investigated through the SEM images. In chemical method, FeCl3 was used as an oxidant for polymerization of pyrrole. It was observed that polypyrrole nucleated at random positions within the pores of the membrane and grew until it reached a pore wall or another polypyrrole mass because there were no molecular anchor sites on the alumina pore walls and therefore the shape of polypyrrole nanostructures was a linear aggregate of close-packed irregular blobs.

For electrochemical synthesis of polypyrrole nanowires, a thin layer of Au was sputtered on one surface of the membrane to act as the working electrode. In this condition, the polypyrrole had started to grow from the conductive Au layer at the pores bottom and consequently the polypyrrole nanowires were not composed of continuous blobs and their surfaces were smooth. By interrupting the synthesis process before complete filling of the pores, only a fraction of the pores were filled with polypyrrole in the electrochemical route, but in the chemical method, uncontinuous polypyrrole blobs were formed along the nanochannels.

The effect of pressure on the trans-gauche equilibrium of n-butane in water: Relevance to pressure denaturation of proteins

KATO, Minoru (College of Pharmaceutical Sciences, and Graduate School of Science and Engineering, Ritsumeikan University) ; KASEZAWA, Kunihiro (Graduate School of Science and Engineering, Ritsumeikan University)

The hydrophobic interaction has been thought to be an important factor governing the structural stability of proteins. This commonly held view derives from the good correlation between the thermodynamics for the transfer of hydrophobic molecules from a hydrophobic liquid to water and for the thermal denaturation of proteins. That is, the dominant factor for the thermodynamic stability of proteins is due to the assembly of the hydrophobic side chains in the interior of proteins. However, it is well-known that this model is inconsistent with pressure denaturation. Using information theory, Hummer et al. (PNAS, 1998) showed that pressure stabilizes the solvent-separated minimum in the potential of mean force between two methane molecules in water. The authors suggested that pressure denaturation was to the result of the penetration of water into the hydrophobic core of the protein. However, this methane dimerization model is experimentally unsuitable because of the experimental difficulty. The trans-gauche equilibrium of butane is an analogous model system. This is because the approaching the methyl groups is associated with the change from the trans to the gauche conformation and is similar to the dimerization of methane. In the present study, we performed a Raman study of pressure effect on the trans-gauche equilibria of n-butane in aqueous and organic solvents. We determined the volume difference between the conformers in various solvents. We discuss the effect of the hydrophobic hydration on the volume difference by comparison with the results in organic solvent. Finally, we compared the present result to the case of the dimerization of methane in water, and address the relevance to the pressure denaturation of proteins.

Colloidal porous nanoparticles of vermiculite

MIRZAEV, Sirojiddin (Heat Physics Department Uzbek Academy of Sciences) ZIYAYEV, Gafurjon (Heat Physics Department Uzbek Academy of Sciences)

Colloidal porous hosts in the form of microporous vermiculite ($(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$) is attractive material for a wide range of potential applications. . However, many fundamental challenges still remain in this research field. The work focuses on overcoming some of the present limitations by developing new concepts for the synthesis and functionalization of porous nanoparticles. Vermiculite is a natural mineral that expands with the application of heat. The expansion process is called exfoliation. The exfoliated row material was used to obtain nanoparticles of vermiculite. In current researches diverse group of the scientists is using various methods: electrochemical, chemical, wet-chemical, and etc. We have used sonochemical synthesis to obtain nanoparticles. The synthesis of nanoparticles by using ultrasound radiation has several benefits than other methods. Less cost, simpler devices, most importantly, existence of opportunity for the control of particles sizes lead to increase of the degree of using this method. On the other hand, reason of coming out nanosize particles after ultrasound radiation is still unknown and in this method the final particles shape also unpredictable. Many new applications also first became possible after achieving further control at the nanolevel, i.e., by limiting the particle size of the porous hosts from micrometer- sized bulk materials to nanoparticles. Such a drastic decrease in size leads to fundamental changes in many physical aspects of the porous hosts, including colloidal stability, thermophysical properties, and diffusion path lengths. The effects the irradiation time and reaction temperature on the size of nanoparticles were studied. Using the ultrasonic method can achieve high dispersion of virtually all materials used in nanotechnology.

Scaled particle theory for one- and two- dimensional hard-core fluids in disordered porous matrices

HOLOVKO, Myroslav (Institute for Condensed Matter Physics, National Academy of Sciences, 1 Svientsitskii Street, 79011 Lviv, Ukraine) ; PATSAHAN, Taras (Institute for Condensed Matter Physics, National Academy of Sciences, 1 Svientsitskii Street, 79011 Lviv, Ukraine) ; DONG, Wei (Laboratoire de Chimie, UMR 5182 CNRS, Ecole Normale Supérieure de Lyon, 46, Allée d'Italie, 69364 Lyon Cedex 07, France)

The scaled particle theory is known as an excellent tool for the description of thermodynamic properties of hard-core particle systems. Our recent results show an applicability of this theory to a study of hard sphere fluid confined in disordered hard sphere matrices [1, 2]. Moreover, it is possible to extend the approach proposed in these studies to the case of one- and two-dimensional systems [3]. The corresponding generalization is presented in the given report and analytical expressions for the chemical potential of a confined hard-core fluid are compared numerically with Monte-Carlo simulation results in the different dimensions. Also the most recent improvements of the theory are discussed within this study.

[1] Holovko M., Dong W., J. Phys. Chem. B 133 (2009) 6360. [2] Patsahan T., Holovko M., Dong W., J. Chem. Phys. 134 (2011) 074503. [3] Holovko M., Dong W., Shmotolokha V., Condens. Matter Phys. 13, 23607 (2010).

Molecular simulation of fluid-solid interface at nanoscale

OULD-KADDOUR, Fouzia (Laboratoire de physique theorique, Faculte des Sciences, Universite Abou-Bakr Belkaid de Tlemcen Algerie)

The equilibrium states of vapor and liquid coexistent phases in contact with a solid surface are studied at the nanoscale by molecular dynamics simulations for a temperature close to the fluid triple point.The characteristics of the solid-fluid interfaces are determined when the interaction strength between the fluid and the solid varies in order to go from a situation of complete drying to that of complete wetting. From the vapor-liquid density profiles of liquid drops lying on the substrate surface or minisci of liquid films confined in slit pores, the contact angles made by the vapor-liquid interface with the solid are computed. The angle values are found in good agreement with the estimates obtained through the Young's relation from the surface tensions associated to the vapor-solid, liquid-solid and vapor-liquid interfaces. The uncertainties inherent to the angle computation are found to be around few degrees.

Thermodynamic approach of actinides solvation and extractionby N,N-dialkylamide

RODRIGUES, Florian (CEA), Marie-Christine Charbonnel, Nathalie Boubals, Nicole Morel-Desrosiers et Jean-Pierre Morel

In the frame of nuclear field reprocessing, the recovery of major actinides (uranium and plutonium) is the key step. The PUREX process based on the extraction by TBP is the reference way. Among different options studied for the future actinide recycling, the GANEX concept leads on a group actinide extraction. The first step could be the extraction of uranium by dialkylamides (RR'CONR''). Although their efficiency has been studied [1,2], understanding at molecular scale can be improved. The extraction mechanism of actinides by neutral dialkylamides systems is described by: Mm+ (aq) + m NO3- (aq) + 2 A (org) D M(NO3)mA2 (org) The description of this mode by the thermodynamic cycle highlights the need to consider different contributions to ΔextG° of related equilibrium. This macroscopic value can be explained as a sum of energetic and structural terms (ΔextG = ΔextH – T ΔextS), and microcalorimetry is the best method for separate each contribution of extraction enthalpy (energetic term). The global measurement of heat related to the extraction of U(VI) from LiNO3 media by Di-2-ethylhexylbutyramide (DEHiBA) in dodecane was determined by microcalorimetry. As shown by MARCUS [3], this thermal signal is constituted by heat of extraction and numbers of heat effects. Among these additional heats, the dilution of DEHiBA in dodecane was the first phenomena studied. Further investigations were carried out using other methods (NMR, SAXS) to identify the presence of amide aggregation or not [4].

1. Musikas, C. (1988). "Potentiality of Nonorganophosphorus Extractant in Chemical Separations of Actinides." Separation Science and Technology 23(12): 1211-1226. 2. Manchanda, V. (2004). "Amides and diamides as promising extractants in the back end of the nuclear fuel cycle: an overview." Separation and Purification Technology 35(2): 85-103.
3. Marcus, Y. and Z. Kolarik (1973). "Thermodynamics of Liquid-Liquid Distribution Reactions .1. Dioxouranium(Vi) Nitrate-Water-Tri-N-Butyl Phosphate-N-Dodecane System." Journal of Chemical and Engineering Data 18(2): 155-163 4. "Comprehensive organic chemistry", Barton and Ollis, Pergamon Press, Oxford, New-York, Toronto, Sydney, Paris, Frankfurt, Vol. 2, chap. 9.9, 957-1010, "Amides and related compounds", 1979.

List of participants

A

ABREU, Manuela, manuelaabreu@isa.utl.pt, Full professor, Technical University of Lisbon, Instituto Superior de Agronomia, Tapada da Ajuda, 1349, LISBOA, PT

AIZAWA, Hideki, aizawa@pharm.setsunan.ac.jp, Setsunan University, 45-1 Nagaotougemachi, Hirakata City, 5730101, OSAKA, JP

AMATORE, Christian, christian.amatore@ens.fr, Drce cnrs, academie des sciences, ENS, UPMC & CNRS , ENS, Dept de Chimie, UMR 8640, 24 rue Lhomond, 75005, PARIS, FR

AUPIAIS, Jean, jean.aupiais@cea.fr, CEA , CEA DAM DIF, 91297, ARPAJON, FR

B

BAADEN, Marc, baaden@smplinux.de, Charge de recherche cnrs, CNRS , CNRS UPR 9080, 13 rue Pierre et Marie Curie, 75005, PARIS, FR

BARANYAI, András, bajtony@chem.elte.hu, Professor, Inst. Chemistry, Eötvös Univ. , Eötvös Univ., Pázmány P.s. 1/A, 1117, BUDAPEST, HU

BARTCZAK, Martyna, mbartczak@mitr.p.lodz.pl, Ph.d. student, Institute of Applied Radiation Chemistry, Technical University of Lodz , Zeromskiego 116, 90-924, LODZ, PL

BERNARD, Olivier, olivier.bernard@upmc.fr, Doctor, UPMC-laboratoire PECSA, 4, place Jussieu, Bat. 74, C.C. 51, 75005, PARIS, FR

BESTER-ROGAC, Marija, marija.bester@fkkt.uni-lj.si, University of Ljubljana , Askerceva 5, 1000, LJUBLJANA, SI

BHOWMIK, Debsindhu, debsindhu.bhowmik@cea.fr, Doctorate student, Laboratoire Léon Brillouin, CEA-Saclay , Laboratoire Léon Brillouin, CEA-Saclay, France, 91191, GIF-SUR-YVETTE CEDEX, FR

BOHINC, Klemen, klemen.bohinc@zf.uni-lj.si, Teacher, Faculty of Health Sciences, UL ZF, Zdravstvena pot 5, 1000, LJUBLJANA, SI

BONCINA, Matjaz, matjaz.boncina@fkkt.uni-lj.si, faculty, Askerceva 5, 1000, LJUBLJANA, SI

BORGIS, Daniel, daniel.borgis@ens.fr, Dr cnrs, CNRS , ECOLE NORMALE SUPERIEURE, Département de chimie - 24 rue Lhomond, 75231, PARIS, FR

BOUGHAMMOURA, Sondès, sondes.mhalla@fsm.rnu.tn, Maître assistante, Faculté des sciences de Monastir, Faculté des sciences, Av Environnement, 5000, MONASTIR, TN

BUCHNER, Richard, richard.buchner@chemie.uni-regensburg.de, Universitaet Regensburg, Institut fuer Physikalische und Theoretische Chemie, Universitaetsstr. 31, 93040, REGENSBURG, DE

C

CHANDRA, Amalendu, amalen@iitk.ac.in, Professor, Indian Institute of Technology Kanpur , Department of Chemistry, Indian Institute of Technology, Kanpur, 208016, KANPUR, IN

CHANG, Chih Hsiang, ccs@itri.org.tw, Researcher/manager, ITRI, Rm.420-1, Bldg.77, 195, Sec.4, Chung Hsing Rd.,Chutung, 31040, HSINCHU, TW

CHARBONNEL, Marie-christine, marie-christine.charbonnel@cea.fr, Group leader, CEA Marcoule, DRCP/SCPS/LILA, BP 17171, 30207, BAGNOLS-SUR-CEZE, FR
CHASSAGNE, Claire, c.chassagne@tudelft.nl, Assistant professor, TU Delft , Stevinweg 1 (Stevin III), k. 0.06, 2628, CN DELFT, NL
CHERGUI, Majed, majed.chergui@epfl.ch, Full professor, head of the , EPFL-SB-ISIC-LSU , CH H1 625, Station 6, 1015, LAUSANNE, CH
COASNE, Benoit, benoit.coasne@enscm.fr, Cnrs , CNRS / Institut Charles Gerhardt Montpellier, 8 rue de l Ecole Normale, 34296, MONTPELLIER, FR
COLOMBANI, Jean, jean.colombani@univ-lyon1.fr, Maître de conférences, Université Claude Bernard Lyon 1, LPMCN, Bât. Brillouin - la Doua, 69622, VILLEURBANNE, FR
COSLOVICH, Daniele, daniele.coslovich@univ-montp2.fr, Université Montpellier 2, Place Eugène Bataillon, 34095, MONTPELLIER, FR
COSLOVICH, Daniele, daniele.coslovich@, Université Montpellier 2 , Place Eugène Bataillon, 34095, MONTPELLIER, FR

D

DINÇ, Saliha, salihadinc@selcuk.edu.tr, SELCUK UNIVERSITY, SELÇUK UNIVERSITY ÇUMRA VOCATIONAL HIGH SCHOOL, CUMHURYET MAH., 42500, KONYA, TR
DELPECH, Sylvie, sylvie-delpech@chimie-paristech.fr, Researcher, CNRS , LECIME-ENSCP, 11 rue P. et M. Curie, 75231, PARIS CEDEX 05, FR
DEWEN, Zeng, dewen_zeng@hotmail.com, Professor, Central South University , College of Chemistry and Chemical Engineering, Central South University, 410083, CHANGSHA, CN
DUBEY, Chandra, chandramohandubey@gmail.com, glb , mtre, 281101, IN
DUBOIS, Emmanuelle, emmanuelle.dubois@upmc.fr, Dr, UPMC PECSA, 4 place Jussieu, case 51, 75005, PARIS, FR
DUFRêCHE, Jean-françois, jean-francois.dufreche@icsm.fr, Professeur, Université Montpellier 2, ICSM Centre de Marcoule, Bat426, 17171, BAGNOLS SUR CEZE, FR
DUVAIL, Magali, magali.duvail@upmc.fr, Post doct, ANDRA / CNRS UPMC , Laboratoire PECSA UMR 7195 - UPMC, 4 place Jussieu - case 51, 75252, PARIS CEDEX 05, FR

F

FADEEVA, Yuliya, jaf@isc-ras.ru, Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya St., 1, 153045, IVANOVO, RU
FALLAHI, Afsoon, afsoonfalahi@gmail.com, Phd student, aut , hafez ave., 0098, 21, IR
FARJAM, Mohammad Hosein, farjam@iauf.ac.ir, Student, Islamic azad university,firoozabad brabch , shahid aghaii street, 7185787193, SHIRAZ, IR
FEDOTOVA, Marina, mvf@isuct.ru, Leading researcher, Institute of Solution Chemistry of Russian Academy of Sciences , Academicheskaya st., 1, 153045, IVANOVO, RU
FERRIER, Mariette, mariette.ferrier@cea.fr, CEA, CEA Marcoule , BP 171 , 30207, FR
FERRU, Geoffroy, geoffroy.ferru@cea.fr, Thésard, CEA , CEA Marcoule - DEN/DRCP/SCPS/LILA, BP 17171 - Batiment 181, 30207, BAGNOLS SUR CEZE, FR

G

GAILLARD, Clotilde, c.gaillard@ipnl.in2p3.fr, IPNL - CNRS, bat. Dirac , 4 rue Enrico Fermi, 69622, VILLEURBANNE, FR

22 D

GAMSJAEGER, Heinz, gamsjaeg@unileoben.ac.at, Emeritus professor of physical chemistry, Chair of Physical Chemistry, Montanuniversitaet Leoben , Franz-Josef-Strasse 18, A 8700, LEOBEN, AT

GHANBARI, Mohammad Mehdi, m.mehdi.ghanbari@gmail.com, Islamic Azad University Sarvestan Branch, Sarvestan, Islamic Azad University Sarvestan Branch, 73451, 173, IR

GOMAR, Jérôme, jgomar@rd.loreal.com, L'OREAL, 1 avenue eugène schueller, 93600, AULNAY SOUS BOIS, FR

GóMEZ-ESTéVEZ, Juan Luis, jlgomez@ffn.ub.es, Professor titular, Universitat de Barcelona , Dept. Física Fonamental Facultat Física, Diagonal,647, E-08028, BARCELONA, ES

GONCHARUK, Vladyslav, honch@iccwc.kiev.ua, Academician-secretary (head) of chemistry division of national academy of sciences of ukraine, director of a.v.dumansky institute of colloid and water chemistry of nas of ukraine, National Academy of Sciences of Ukraine, A.V.Dumansky Institute of Colloid and Water Chemistry of NAS of Ukraine , 42 Vernadsky blvd., Kyiv-142, 03680, Ukraine, 03680, KYIV, UA

GUILBAUD, Philippe, philippe.guilbaud@cea.fr, Dr, CEA, DEN/MAR/DRCP/SCPS/LILA, Bat 181, CEA Marcoule - BP 17171, F-30207, BAGNOLS SUR CEZE , FR

H

HAJIMOHAMMADPOOR, Maryam, maryammohammadpoor@yahoo.com, University College Dublin, Belfield, D4, DUBLIN, IE

HEFTER, Glenn, g.hefter@murdoch.edu.au, Murdoch University, CMS, Murdoch University, South Street, WA-6150, MURDOCH, AU

HIRATA, Fumio , hirata@ims.ac.jp, Professor, Institute for Molecular Science, Nishigonaka 38, Myodaijicho, 444-8585, OKAZAKI, JP

HOLOVKO, Myroslav, holovko@icmp.lviv.ua, Head of department , Institute for Condensed Matter Physics of NAS of Ukraine, 1,Svientsitskii Street, Institute for Condensed Matter Physics, 79011, LVIV, UA

I

IAKYMOVA, Tetiana, tiyakimova@iccwc.kiev.ua, Senior researcher, A.V.Dumansky Institute of Colloid and Water Chemistry of National Academy of Sciences of Ukraine , 42 Vernadsky blvd., Kyiv-142, 03680,Ukraine, 03680, KYIV, UA

IBUKI, Kazuyasu, kibuki@mail.doshisha.ac.jp, Doshisha University , 1-3 Tatara-Miyakodani, 610-0321, KYO-TANABE, JP

IMAI, Takashi, takashi.imai@riken.jp, RIKEN QBiC, 7-1-26 Minatojima-minamimachi, Chuo-ku, 650-0047, KOBE, JP

INADA, Taeko, tinada-@kitasato-u.ac.jp, Kitasato University , 1-15-1 Kitasato Minamiku, 2520329, SAGAMIHARA, JP

IONKOVA, Iliana, ionkova@pharmfac.acad.bg, Prof., Faculty of Pharmacy , 2 Dunav Str., 1000, SOFIA, BG

IVANOV, Evgeny, evi@isc-ras.ru, Senior research officer, Institute of solution Chemistry of Russian academy of Sciences , 1 Akademicheskaya Street, 153045, IVANOVO, RU

J

JARDAT, Marie, marie.jardat@upmc.fr, UPMC, UMR 7195 PECSA, Case courrier 51, 4 place Jussieu, 75005, PARIS, FR

18 4

JOHANSSON, Charles, charles.johansson@slu.se, Phd-student, Chemistry, SLU , Arrheniusplan 8, 75007, UPPSALA, SE

JUMEAN, Fawwaz, fjumean@aus.edu, Professor, American University of Sharjah , American University of Sharjah, POB 26666, SHARJAH, JO

K

KALAGAEV, Ivan, kalagaev@inbox.ru, Nizhny Novgorod State Technichal University, Nizhny Novgorod region, Tsiolkovsky avenue, 39-99, 606029, DZERSINSK, RU

KALINICHEV, Andrey, kalinich@subatech.in2p3.fr, Directeur de recherche, Ecole des Mines de Nantes , Ecole des Mines de Nantes, 4 rue Alfred Kastler, 44301, NANTES, FR

KAMEDA, Yasuo, kameda@sci.kj.yamagata-u.ac.jp, Professor, Yamagata University, 1-4-12 Kojirakawa-machi, 990-8560, YAMAGATA, JP

KANAKUBO, Mitsuhiro, m-kanakubo@aist.go.jp, Senior researcher, AIST, 4-2-1 Nigatake, Miyagino-ku, Sendai, 983-8551, JP

KANZAKI, Ryo, kanzaki@sci.kagoshima-u.ac.jp, Kagoshima University , 1-21-35, Korimoto, Kagoshima, 8900065, KAGOSHIMA, JP

KATO, Minoru, kato-m@ph.ritsumei.ac.jp, Professor, Ritsumeikan University , 1-1-1 Noji-Higashi, 525-8577, KUSATSU, JP

KHARAT, Sanjeevan, ksanjeevan@dataone.in, Associate professor, H.P.T. Arts and R.Y.K. Science College, Nashik-5, Prin. T. A. Kulkarni, Vidyanagar, Nashik, NASHIK-422005, IN

KISELEV, Michael, mgk@isc-ras.ru, Senior researcher, Institute of Solution Chemistr , Akademicheskaya st.1, 153045, IVANOVO, RU

KLEIN, Michael, mlklein@temple.edu, Director icms, Temple University, 1900 North 34th Street, Bio-Life Building, 113, 19122, PHILADELPHIA, PA, US

KOBAYASHI, Michio, michio@chem.aoyama.ac.jp, Professor, Aoyama Gakuin University , Fuchinobe, Sagamihara, Kanagawa, 252-5258 Japan, 252-5258, SAGAMIHARA, KANAGAWA, JP

KODAMA, Daisuke, dkodama@chem.ce.nihon-u.ac.jp, Associate professor, Nihon University , 1 Nakagawara Tokusada Tamura-machi, 963-8642, KORIYAMA, FUKUSHIMA, JP

KOLKER, Arkady, amk@isc-ras.ru, Deputy derector, Insitute of Solution Chemistry RAS, Akademicheskay str., 1, 153045, RU

KOVALENKO, Andriy, andriy.kovalenko@nrc-cnrc.gc.ca, Group leader - theory & modeling, National Institute for Nanotechnology, 11421 Saskatchewan Drive, T6G 2M9, EDMONTON AB, CA

KUNZ, Werner, werner.kunz@chemie.uni-regensburg.de, Hed of institute, Faculty of Chemistry and Pharmacy , University of Regensburg, 93040, REGENSBURG, DE

LáSZLó, Túri, turi@chem.elte.hu, Institute of Chemistry, Eötvös Loránd University, Pázmány Péter s. 1/a, H-1117, BUDAPEST, HU

L

LECOMTE, Michaël, michael.lecomte@cea.fr, CEA, CEA Marcoule , BP 171, 30207, FR

LEGUAY, Sébastien, leguay@ipno.in2p3.fr, Phd student, CNRS , 43 Avenue du Président salvador Allende, 91300, MASSY, FR

LILEEV, Alexaner, lilaser@mail.ru, Professor, Moscow State University of Environmental Engineering, Leninsky prosp. Bd.62, app. 238, 119296, MOSCOW, RU

20 6

LOZADA-CASSOU, Marcelo, marcelo@imp.mx, Research program director, Mexican Petroleum Institute , Eje Central Lazaro Cardenas Norte 152, Programa de Ingeniería Molecular, 07730, MEXICO, MX

LUNDBERG, Daniel, daniel.lundberg@slu.se, Researcher, Swedish University of Agricultural Sciences, P.O. Box 7015, 75649, UPPSALA, SE

LYASHCHENKO, Andrey, aklyas@mail.ru, Head of laboratory, Institute Jenaral @ Inorganic Chemistry RAS , Moscow, Leninsky pr., 31, IGIC RAS, Russia, 119991, MOSCOW, RU

M

MADDEN, Paul, paul.madden@queens.ox.ac.uk, Provost, University of Oxford , The Queen's College, High Street, OX14AW, OXFORD, GB

MAGALHAES, Clara, mclara@ua.pt, University of Aveiro , University of Aveiro, Campus de Santiago, 3810, AVEIRO, PT

MAHLER, Johan , johan.mahler@slu.se, Phd student, Chemistry, SLU , Kemininstitutionen, Arrheniusplan 8, 75007, UPPSALA, SE

MANTECA, Consolación, consolacion.manteca@upm.es, Profesor titular de universidad, Universidad Politécnica de Madrid, Plaza de Cardenal Cisneros n°3, 28040, MADRID, ES

MARCUS, Yizhak, ymarcus@vms.huji.ac.il, Prof., Hebrew University, Institute of Chemistry, Edmund Safra Campus, 91904, JERUSALEM, IL

MASAKI, Okada, etj1502@mail4.doshisha.ac.jp, Doshisha university , Kyotohu kyotanabeshi tataramiyakodani 1-3, 618, 91, JP

MéRIGUET, Guillaume, guillaume.meriguet@upmc.fr, Assistant professor, UPMC - Lab PECSA , case 51, 4 place Jussieu, 75005, PARIS, FR

MHALLA, Jalel, jalel.mhalla@fsm.rnu.tn, Professor, Faculté des sciences de Monastir, Faculté des sciences, Av Environnement, 5000, MONASTIR, TN

MIKELIC, Andro, mikelic@univ-lyon1.fr, INSTITUT CAMILLE JORDAN, 43 bvd 11novembre, 69100, VILLEURBANNE, FR

MOREL, Jean-pierre, j-pierre.morel@univ-bpclermont.fr, Professor emeritus, Blaise Pascal University, Chimie Bât. 7, 24 avenue des Landais, B.P. 80026, 63171, AUBIERE CEDEX, FR

MOREL-DESROSIERS, Nicole, nicole.morel@univ-bpclermont.fr, Professor, Blaise Pascal University, Chimie Bât. 7, 24 avenue des Landais, B.P. 80026, 63171, AUBIERE CEDEX, FR

MORISAWA, Yusuke, morisawa@kwansei.ac.jp, Postdoctoral fellow, Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, 6691337, SANDA, JP

N

NERUKH, Dmitry, d.nerukh@aston.ac.uk, Aston University, Aston Triangle, B47ET, BIRMINGHAM, GB

NEZBEDA, Ivo, ivonez@icpf.cas.cz, Professor and chair, Academy of Sciences, Inst. Chem. Process Fund., Rozvojova 135, 16502, PRAGUE 6, CZ

NOVIKOVA, Svetlana, sveta.novikova@gmail.com, Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences, 34 Oktyabrskaya av., apt. 50, 630007, NOVOSIBIRSK, RU

NURYONO, Nuryono, nuryono_mipa@ugm.ac.id, Lecturer, Departement of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, PO Box Bls 21, Sekip Utara, 55281, YOGYAKARTA, ID

19 2

O

OH, Taehwan, taehwanoh@ynu.ac.kr, Yeungnam University, 103-2207 Taewang Worldheights , Wooksudong, Susunggu, 706920, DAEGU, KR

OLIYNYK, Oleksandr, oleksandr.oliynyk@ens.fr, Cr, ENS , 24 rue Lhomond, 75005, PARIS, FR

OMIDVAR, Hamid, omidvar@aut.ac.ir, Assistant prof, Amirkabir university of technology, 423, Av Hafez, 19957, TEHRAN, IR

OTSUKA, Takuhiro, takutaku777@hotmail.com, Tokyo Institute of Technology, 2-12-1-W4-14 O-okayama, Meguro-ku, 152-8551, TOKYO, JP

P

PALINKAS, Gabor, palg@chemres.hu, General director, Chemical Research Center, Pusztaszeri ut 59, 1025, BUDAPEST, HU

PAPAICONOMOU, Nicolas' Hotel part, nicolas.papai@gmail.com, Assistant professor, University of Savoie , LCME - Batiment Chartreuse, Université de Savoie - Technolac , 73376 , LE BOURGET DU LAC CEDEX, FR

PARASKOVA, Julia, julia.paraskova@kemi.uu.se, Uppsala University, Analytical Chemistry, P.O. Box 599, 75124, UPPSALA, SE

PAREZ, Stanislav, parez@icpf.cas.cz, Ph.d. student, Institute of Chemical Process Fundamentals of the ASCR, Prague , Rozvojova 2/135, Prague 6 - Suchdol, CZ, 165 02, CZ

PERSSON, Ingmar, ingmar.persson@slu.se, Professor, Swedish University of Agricultural Sciences, Department of Chemistry, SLU, P.O.Box 7015, 750 07, UPPSALA, SE

PREDOTA, Stanislav, stanislav.parez@seznam.cz, Ph.d. student, Institute of Chemical Process Fundamentals, Rozvojova 135, 16502, PRAGUE 6, CZ

R

REA, Anita, anita.rea@syngenta.com, Physical chemist, Syngenta , Syngenta, Jealotts Hill International Research Centre, RG42, 6EY, GB

RENAUDIN, Laëtitia, laetitia.renaudin@cea.fr, CEA Saclay, Centre d'études de Saclay, 91191, GIF SUR YVETTE, FR

RENAULT, Jean Philippe, jprenault@cea.fr, CEA, Bat. 546, 91191, GIF/YVETTE, FR

RIVEROS SANTOYA, Diana Carolina, caro-riv@uniandes.edu.co, Magister student, Universidad de los Andes, Cra 1 # 18 A 10, 11111, BOGOTA, CO

RODRIGUES, Florian, florian.rodrigues@cea.fr, CEA, CEA, Marcoule, DEN/DRCP/SCPS/LILA, BP 17171, 30207, BAGNOLS-SUR-CEZE, FR

ROONEY, David, d.rooney@qub.ac.uk, Doctor, Queen's University Belfast, University Road, Belfast, BT7 , 1NN, GB

ROTENBERG, Benjamin, benjamin.rotenberg@upmc.fr, CNRS and UPMC, Laboratoire PECSA, CC51, UPMC, 4 place Jussieu, 75005, PARIS, FR

ROWLAND, Darren, d.rowland@murdoch.edu.au, Phd student, Murdoch University, Western Australia, South St, 6150, MURDOCH, AU

S

SADAKANE, Koichiro, sadakane@post.kek.jp, Postdoctoral fellow, High Energy Accelerator Research Organization, 203-1 Shirakata, Tokai, 3191106, IBARAKI, JP

SADEGHI, Rahmat, rahsadeghi@yahoo.com, University of Kurdistan , Department of Chemistry, University of Kurdistan, Sanandaj, Iran, SANANDAJ, IR

192

SAFONOVA, Liubov, lps@isc-ras.ru, Institute of Solution Chemistry of RAS, Akademicheskaya str., 1, 153045, IVANOVO, RU

SALAMANCA BLANCO , Yina Patricia , ypsalamancab@unal.edu.co, Ph.d student , Universidad Nacional de Colombia , Cll 71 C ·No 94 A 72 Int 1 Apto 503, 11111, BOGOTÃ D.C., CO

SALANNE, Mathieu, mathieu.salanne@upmc.fr, UPMC, Laboratoire PECSA - CC51, 4 place Jussieu, 75005, PARIS, FR

SCHOTT, Marc-alexandre, marc-alexandre.schott@univ-montp1.fr, CNRS - IBMM, Artificial Biopolymers Department, MONTPELLIER, Faculté de Pharmacie, 15 avenue Charles Flahault, 34093, MONTPELLIER, FR

SHALAEV, Evgenyi, evgenyi.y.shalaev@pfizer.com, Pfizer Inc, Eastern Point Rd, 06340, GROTON, CT, US

SHIN, Irina, irina.shin@weizmann.ac.il, Weizmann Institute of Science, Sokolov st., 8, 75445, REHOVOT, IL

SHMUKLER, Liudmila, les@isc-ras.ru, Researcher, Institute of Solution Chemistry, Akademicheskaya, 1, 153045, IVANOVO, RU

SIBIK, Juraj, js927@cam.ac.uk, Phd student, University of Cambridge, Gonville and Caius College, Trinity Street, CB2 1TA, CAMBRIDGE, GB

SIBOULET, Bertrand, bertrand.siboulet@cea.fr, CEA/ICSM , bat426, CEA Marcoule, 30207, BAGNOLS SUR CEZE, FR

SONG, Xuedan, song@chem.kyushu-univ.jp, department of chemistry, faculty of science, kyushu university, 6-10-1 hakozaki, higashi-ku, 812-8581, FUKUOKA, JP

SPEZIA, Riccardo, riccardo.spezia@univ-evry.fr, Cnrs , CNRS - Université d'Evry Val d'Essonne, Bd F. Mitterrand, 91025, EVRY, FR

STAFIEJ, Janusz, jstafiej@ichf.edu.pl, Adiunkt, Institte of Physical Chemistry, Kasprzaka 44/52, 01-224, WARSAW, PL

STILBS, Peter, stilbs@kth.se, Professor, Royal Institute if Technology, Physical Chemistry, Teknikringen 36, SE-10044, STOCKHOLM, SE

SVIR, Irina, irina.svir@ens.fr, Dr, ENS, 24 rue Lhomond, 75005, PARIS, FR

T

TAURA, Toshiaki, taura@ist.aichi-pu.ac.jp, Professor, University of Aichi Prefecture, Kumabari, Nagakute, 480-1198, AICHI, JP

TEIXEIRA, Jose, jose.teixeira@cea.fr, Directeur de recherche, CNRS, Lab. Leon Brillouin, CEA Saclay, 91191, GIF-SUR-YVETTE, FR

TERAZIMA, Masahide, mterazima@kuchem.kyoto-u.ac.jp, Professor, Kyoto University , Sakyo-ku, 606-8502, KYOTO, JP

THIS, Hervé, herve.this@paris.inra.fr, Chimist , CEA, AgroParisTech, 16 rue Claude Bernard, 78530, PARIS, FR

THOMAS, Zemb, thomas.zemb@icsm.fr, Director of umr 5257, Commissariat à l'Energie Atomique (CEA), CEA/MARCOULE - Bat 426 ICSM, BP 17171, 30207, BAGNOLS SUR CEZE CEDEX, FR

TOIKKA, Maria, masha-toikka@yandex.ru, Phd, Saint-Petersburg State University , Serebristy bulvar 37-121, 197341, SAINT-PETERSBURG, RU

TOMAS, Renato, rtomas@ktf-split.hr, Assistant professor, Faculty of Chemistry and Technology, University of Split, Nikole Tesle 10/V, 21000, SPLIT, HR

21 2

TOMINAGA, Toshihiro, tominaga@dac.ous.ac.jp, Professor, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama, 700, 5, JP

TOWEY, James, pyjjt@leeds.ac.uk, University of Leeds , Physics and Astronomy, E.C. Stoner Building, University of Leeds, Woodhouse Lane, LS49JT, LEEDS, GB

TROKHYMCHUK, Andrij, adt@icmp.lviv.ua, Institute for condensed matter physics, Svientsitskoho 1, 79011, LVIV, UA

TSURKO, Jelena , jelena.n.tsurko@univer.kharkov.ua, Higher scientific researcher , V.N.Karasin National University Kharkiv, Scientific Research Institute for Chemistry , Svoboda Pl.4, 61077 , KHARKIV , UA

U

UHRIKOVA, Daniela , uhrikova@fpharm.uniba.sk, Assoc. professor, Faculty of Pharmacy, Comenius University, Faculty of Pharmacy Comenius University, Odbojarov 10, 83232, BRATISLAVA, SK

UMEBAYASHI, Yasuhiro, yumeb@chem.kyushu-univ.jp, Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, 812-8581, FUKUOKA, JP

V

VARGAS ESCAMILLA, Edgar Francisco , edvargas@uniandes.edu.co, Professor , Universidad de los Andes , Cra 1 No18 A 70 , 11111, BOGOTÃ D.C, CO

VITORGE, Pierre, pierre.vitorge@cea.fr, CEA & UMR 8587 , CEA, Saclay, DEN, DPC, SECR, LSRM, Bat.391, 91191, GIF-SUR-YVETTE, FR

VLACHY, Vojko, vojko.vlachy@fkkt.uni-lj.si, Professor, University of Ljubljana , Fakulty of Chemistry and Chenical Technology, Askerceva 5, 1000, LJUBLJANA, SI

VOIGT, Wolfgang, wolfgang.voigt@chemie.tu-freiberg.de, Prof. dr., TU Bergakademie Freiberg , TU Bergakademie Freiberg, Leipziger Str. 29, 09596, FREIBERG, DE

VUILLEUMIER, Rodolphe, rodolphe.vuilleumier@ens.fr, ECOLE NORMALE SUPERIEURE, Département de chimie de l'ENS - 24 rue Lhomond, 75005, PARIS, FR

W

WADA, Ryoichi, rc009047@ed.ritsumei.ac.jp, Ritsumeikan University, Satonaka-cho 2-2-2-405, 663-8183, NISHINOMIYA, JP

WAGHORNE, Earle, earle.waghorne@ucd.ie, University College Dublin, Belfield, D4, DUBLIN, IE

Y

YAMAGUCHI, Toshio, yamaguch@fukuoka-u.ac.jp, Professor, Fukuoka University , Nanakuma, Jonan-ku, 814-0180, FUKUOKA, JP

YAMAZAKI, Takeshi, takeshi@ualberta.ca, National Institute for Nanotechnology, 11421 Saskatchewan Drive, T6G0T5, EDMONTON, CA

155

Organising Committee

Chairman:
Pierre TURQ, Université Pierre & Marie Curie, Paris / ICSM

Vice-chairpersons:
Isabelle BILLARD, CNRS, Strasbourg
Jean-François DUFRECHE, Université Montpellier II / ICSM
Michaël LECOMTE, CEA Marcoule.

Local Committee:

Chairman:
Christian BONNET, CEA Marcoule
Conference secretary:
Mariette TUFFERY, CEA Marcoule.
assisted by Eva RECORDIER, CEA Marcoule.

Scientific Committee

Chairwoman:
Nicole MOREL-DESROSIERS, Université Blaise Pascal, Clermont-Ferrand
Scientific secretary:
Bertrand SIBOULET, CEA Marcoule / ICSM

International Steering Committee

Chairman:
I. PERSSON, Uppsala, Sweden
Vice-chairpersons:
G. HEFTER, Murdoch, Australia,
B. RODE, Innsbruck, Austria,
P. TURQ, Paris, France,
T. YAMAGUCHI, Fukuoka, Japan,
J. BARTHEL, Regensburg, Germany,
B. GILL, Leeds, United Kingdom