Toshio Yamaguchi

PROGRAM AND ABSTRACTS

ICSC

30th International Conference on Solution Chemistry

Murdoch University
Perth, Australia

July 16 – 20
2007

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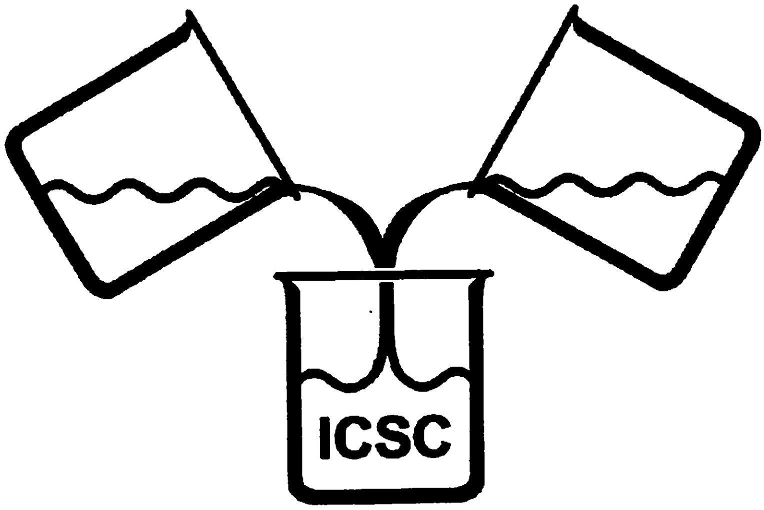
UNIVERSITY
PERTH, WESTERN AUSTRALIA

PROGRAM AND ABSTRACTS



30th International Conference on Solution Chemistry

Perth, Australia

2007

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Tuesday, 17th July

9.00	**Plenary Lecture (ECL2; Chair: Marsh)** Doug MacFarlane *Ionic Liquids – Novel Solvents for Green Chemistry, Electrochemistry and Biological Chemistry*	
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11.50	Marija Bešter-Rogač *Thermodynamics of Micellization of Non-Ionic and Ionic Surfactants & Their Structural Properties in Aqueous Solution*	
12.10	Wolfgang Wachter *How Co-Ions Influence the Stability of Ionic Microemulsions*	Natallia Torapava *Structure Determination of Hydrated, Hydrolyzed and Solvated Thorium(IV) Ions in Solution and Solid State*
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14.20	**Keynote Lecture** Toshio Yamaguchi *On the Role of Solvent Environment in Alcohol-induced α-Helix Formation of Model Peptides*
15.00	Ingmar Persson *Structure of the Hydrated Lanthanoid(III) Ions in Aqueous Solution Determined by EXAFS Spectroscopy*
15.20	Alan Soper *Structure Refinement Methods Applied to Neutron and X-Ray Diffraction Data on Water and Aqueous Solutions*
15.40	AFTERNOON TEA
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Friday, 20th July

9.00	✓**Plenary Lecture (ECL2; Chair: Yamaguchi)** Ken Marsh *Ionic Liquids: Are they Salts or High Boiling Organic Liquids?*	
	Ionic Liquids – 2 (ECL2; Chair: Yamaguchi)	**Thermodynamics & Kinetics – 3 (ECL4; Chair: Magalhães)**
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10.40	✓Ken Harris *Transport Properties of Ionic Liquids at High Pressure*	
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	Ionic Liquids – 2 (ECL2; Chair: Takamuku)	**Thermodynamics & Kinetics – 3 (ECL4; Chair: Sandström)**
11.30	Kenta Fujii *Conformational Equilibrium of Bis(fluoroslufonyl) Imide Anion in Room-Temperature Ionic Liquid*	Masaaki Tabata *Solvent Composition Effects on Relaxation of Bulk Water Molecules and on Water Molecule Exchange Reaction of Aquanickel(II) in Aqueous Mixed Solvents with 2-Propanol or 1-Propanol*
11.50	Ryo Kanzaki *Acidity and Basicity of Ionic Liquids of Onium Salt*	Imre Tóth *Naked Tl-Pt Bonded Cyano Complexes: New Results*
12.10	Ika Oktavianawati *Xylanase-Hydrolyzed Reaction on Xylan in Ionic Liquids*	Masahide Terazima *Time-Resolved Enthalpies, Heat Capacities and Translational Diffusion of Reaction Intermediates of Biological Proteins*
12.30	Junhua Huang *Analysis of Ionic Motions in Plastic Crystals by Dielectric Response*	Deresh Ramjugernath *Estimation of the Vapour Pressure of Organic Compounds by a Group Contribution Method*
12.50	**CLOSING CEREMONY (ECL2)**	
13.15	**FINISH**	

PLENARY and KEYNOTE PRESENTATIONS

(Presenters listed in alphabetical order)

Modelling the Shape and Phase of Nanoparticles in Solution

Amanda S. Barnard

Department of Materials, University of Oxford, Oxford, OX1 3PH, UK.

It has been widely shown that many fundamental properties of nanomaterials have a strong dependence on size, or more specifically, on the physical extent in characteristic dimension(s). Although great advances have been made in controlling the size (and size dispersion) of collections of nanomaterials, variations of some properties still remain due to a dependence on the nanomorphology, characterized by the crystallographic phase and the geometric shape. Individual properties such as quantum confinement, nanomagnetism, and catalytic properties have been found to be shape dependent, as have collective properties such as the self-assembly and degree of dispersion or agglomeration[1]. Therefore, it is clear that the nanomorphology must be carefully controlled to reliably synthesize large quantities of nanoparticles with uniform properties. This is an ideal problem for synthetic chemistry, since many chemical factors such as temperature, composition, and choice of surfactants are know to directly influence nanomorphology in a relatively predictable way. It is also an ideal problem for theory and simulation[1], since it is possible to examine the importance of these (and other) factors in a systematic manner, in isolation of other parameters which may be held constant. Presented here are results of a study using a new shape-dependent thermodynamic model[2] to investigate the phase stability of facetted nanoparticles as a function of size[3,4] and chemical environment[4,5]. We will see how simple changes in the surface chemistry can have dramatic effects on shape and dimensional anisotropy, and how this in turn changes the cross-over point for the size-dependent phase transitions.

[1] Barnard, A.S. *J. Mater. Chem.*, **2006**, *16*, 813.

[2] Barnard, A.S.; Zapol, P. *J. Chem. Phys.*, **2004**, *121*, 4276.

[3] Barnard, A.S.; Yeredla, R.R.; Xu, H. *Nanotech.*, **2006**, *17*, 3039.

[4] Barnard, A.S.; Curtiss, L.A. *Nano Lett.*, **2005**, *5*, 1261.

[5] Saponjic, Z.V.; Dimitrijevic, N.; Tiede, D.; Goshe, A.; Zuo, X.; Chen, L.; Barnard, A.S.; Zapol, P.; Curtiss, L.A.; Rajh, T. *Adv. Mater.*, **2005**, *17*, 965; Barnard, A.S.; Saponjic, Z.; Tiede, D.; Rajh, T.; Curtiss, L.A. *Rev. Adv. Mater. Sci.*, **2005**, *10*, 21.

Determination of the Geometric Structure of Ion Hydration Shells within Comprehensive Solute + Solvent Models: An Approach Based on Empirical Potential Structure Refinement of Neutron Scattering Data Combined with X-ray Absorption Spectroscopy

D.T. Bowron [a]* and S. Diaz-Moreno [b]

[a] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK;*
[b] *Diamond Light Source Ltd, Harwell Science and Innovation Campus, Diamond House, Chilton, Didcot, Oxfordshire, OX11 0DE, UK.*

Understanding the detailed structure of ion hydration shells is an important aspect of modern solution chemistry. The information is often essential for developing models of reaction mechanisms. By and large details of ion solvation structure are generally obtained directly through the use of chemically specific local probes such as X-ray absorption spectroscopy, or indirectly using X-ray or neutron diffraction techniques that probe the average structure of a solution. Both these approaches suffer from significant drawbacks. In the case of local structural probes, resulting models are limited to the immediate atomic environment of the ions and often neglect the important role played by the bulk solution structure. In contrast, the global probes are often only weakly sensitive to the precise details of the ion environments and important information is thus often lost in the highly averaged nature of the experimental data. An obvious solution to these difficulties is through the development of comprehensive models that satisfy both the global average and local structural information. Here we present an approach using Empirical Potential Structure Refinement to combine hydrogen-deuterium isotopic substitution neutron scattering results, on the average structure of aqueous solutions, with state-of-the-art X-ray absorption spectroscopy calculations. This method thus allows the ion hydration structures to be evaluated in detail but within the context of a global solution for the structure of the mixture.

What can be learnt from Dielectric Relaxation Spectroscopy about Ion Solvation and Association?

Richard Buchner

Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D–93040 Regensburg, Germany. Richard.Buchner@chemie.uni-regensburg.de

Ion solvation and ion association are key features of ion-solvent interactions and their balance largely determines the structure, thermodynamics and dynamics of electrolyte solutions. Despite being studied for many years with a large number of techniques these effects are still intriguing. Regarding solvation, the discrepancies generally found between effective solvation numbers, as determined from thermodynamic and transport measurements, and the coordination numbers obtained from scattering techniques and simulations, deserve further attention if we are to understand solution properties. For ion association processes, similar discrepancies exist between the results determined by different techniques, which were highlighted at 29ICSC.[1]

The aim of this contribution is to show what kind of information can be provided in this field by dielectric relaxation spectroscopy (DRS) and how this compares with results obtained from other techniques. A short introduction to the principles of DRS, and the analysis of the spectra and its attendant pitfalls, will be given. Solvent-related contributions to the spectrum, which yield effective solvation numbers and information on how the electrolyte affects the dynamics of the bulk solvent, will be considered. Finally, the solute-related part of the spectra will be discussed. From the solute relaxation processes the concentrations of dipolar solute species and – in favourable cases – the kinetics of ion association can be inferred. Detected entities are not only the contact ion pairs accessible with other spectroscopic techniques but additionally – and with even better sensitivity – solvent-shared and solvent separated ion pairs, as well as polar triple ions.

The presentation will be mainly based on examples from 'simple' aqueous and non-aqueous electrolyte solutions. Additionally, polyelectrolytes and micelles of ionic surfactants will also be included to highlight aspects in common with 'simple' electrolytes and to work out features in the relaxation behaviour that are specific to the condensation of counterions on the polyelectrolyte that are typical for such highly-charged systems.

[1] Hefter, G. *Pure Appl. Chem.*, **2006**, *8*, 1571.

Molecular Simulation and Modeling of Water and Aqueous Solutions in Bulk and at Interfaces: From Ambient To Supercritical Conditions

Peter T. Cummings

Department of Chemical Engineering, Vanderbilt University, Nashville, TN 37235–1604
Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831–6496.

In this talk, we review our simulation and theoretical research on water and aqueous solutions, both in bulk and at interfaces (particularly metal oxide interfaces), and at conditions ranging from ambient to supercritical. One research focus has been the development of intermolecular potentials for water. We have had as our goal the development of a polarizable model for water whose bare dipole moment matches that of the isolated water molecule (1.85D), that accurately predicts the structure of water at ambient and supercritical conditions, and that reproduces thermodynamic and dielectric behavior, including the phase envelope. We will describe the evolution of our model from its earliest forms[1] to the latest[2], which achieves many of the goals we set for our model.

We will also review our recent work on the solubility of organics in near-critical water[3], which supports prior theoretical work suggesting that the Gibbs free energy of solvation for longer alkanes is less than that for shorter alkanes at elevate (near supercritical) temperatures. This is a reversal of what is observed at ambient conditions, where the longer alkanes are less miscible with water than shorter alkanes.

Finally, we describe our simulations of water and electrolyte species at metal oxide interfaces. Using a combination of *ab initio* calculations and classical molecular dynamics we have predicted the disstribution of various ionic species as a function of distance from the 110 surface of rutile, and the sites at which the ions adsorb into the surface. These predictions are compared with X-ray standing wave (XRSW) measurements and found to be in remarkably good agreemen[4].

[1] Chialvo, A.A.; Cummings, P.T. *J. Chem. Phys.*, **1996**, *105*, 8274; Chialvo, A.A.; Cummings, P.T. *Fluid Phase Equilibria*, **1998**, *150-151*, 73.

[2] Paricaud, P. et al. *J. Chem. Phys.*, **2005**, *122*, Art. No. 244511; Dyer, P.J.; Cummings, P.T. *J. Chem. Phys.*, **2006**, *125*, Art. No. 144519.

[3] Yezdimer, E.M. et al. *J. Phys. Chem. B*, **2001**, *105*, 841; McCabe, C. et al. *J. Phys. Chem. B*, **2003**, *107*, 12307.

[4] Zhang, Z. et al. *Langmuir*, **2004**, *20*, 4954; Predota, M. et al. *J. Phys. Chem. B*, **2004**, *108*, 12049; *ibid*, **2004**, *108*, 12061; Predota, M. et al. *J. Phys. Chem. C*, **2007**, *111*, 3071; Mamontov, E. et al. *J. Phys. Chem. C*, **2007**, *111*, 4328.

FactSage and ChemApp, Two Tools for the Prediction of Multiphase Chemical Equilibria in Solutions

Gunnar Eriksson

GTT-Technologies, Kaiserstrasse 100, D–52134 Herzogenrath, Germany.

FactSage[1] is an integrated thermochemical databank system consisting of a series of information, database and calculation modules that enable one to access and manipulate pure substance and solution databases. With the various modules one can perform a wide variety of thermochemical calculations, including those of multiphase chemical equilibria, and generate tables, graphs and figures of interest to chemical and physical metallurgists, chemical engineers, corrosion engineers, inorganic chemists, geochemists, ceramists, electrochemists, environmentalists, etc.

Twenty-one Gibbs energy models for condensed, gaseous and aqueous solutions are presently implemented in FactSage. Aqueous models include the Pitzer and Helgeson-Tanger-Shock formalisms, but data and subroutines for concentrated aqueous and non-ideal gaseous phases have also been provided as user-defined by OLI Systems.[2]

The Gibbs-energy minimizer of FactSage is also incorporated into ChemApp,[3] a programmer's library for thermochemistry. Potential applications for the use of ChemApp are almost limitless and include

- using it for the development of application-specific programs, for example to handle repetitive complex equilibrium calculations
- linking it to third-party process simulation packages for modelling new or optimizing existing processes

In the talk the application of user-defined aqueous solution models in FactSage and ChemApp to hydrometallurgical processes, e.g., atmospheric and high-pressure leaching, will be demonstrated.

[1] Bale, C.W.; Chartrand, P.; Decterov, S.A.; Eriksson, G.; Hack, K.; Ben Mahfoud, R.; Melancon, J.: Pelton, A.D.; Petersen, S. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, **2002**, *26*, 189.

[2] www.olisystems.com

[3] www.gtt-technologies.de

Capabilities of Chemical Simulation Methods in the Elucidation of Structures and Dynamics of Solutions

Thomas S. Hofer*, Bernhard R. Randolf, Andreas B. Pribil and Bernd M. Rode

Theoretical Chemistry Division, Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria.

Due to recent methodical developments in connection with enhanced computational capacities theoretical methods have become valuable and reliable tools for the investigation of solutions. Especially simulation techniques utilising a quantum mechanical approach for the treatment of the chemically most relevant region - so-called hybride quantum mechanical/molecular mechanical (QM/MM) simulations - have reached a level of accuracy, in many cases equal or even partly superior to experimental methods. The latter is true whenever ultrafast (i.e. picosecond) dynamics are prevailing such as in labile hydrates or structure breaking systems.

The recent development of an improved QM/MM framework, the Quantum Mechanical Charge Field (QMCF) ansatz[1], allows the elucidation of a broad spectrum of solute systems. As this novel methodology does not require any solute-solvent potential functions, the applicability of the QMCF method is straightforward and universal. This advantage is bought, however, at the prize of a substantial increase of the quantum mechanical subregion, thus boosting computation times to some months up to one year even on parallelising high performance computing clusters.

Molecular Dynamics (MD) simulations of chemical systems showing increasing complexity have been studied demonstrating the superiority of the QMCF ansatz over conventional QM/MM schemes. The systems studied include Pd^{2+}, TiO^{+}, Hg_2^{2+} as well as composite anions such as PO_4^{3-}, SO_4^{2-} and ClO_4^{-}.

[1] Rode, B.M.; Hofer, T.S.; Randolf, B.R.; Schwenk, C.F.; Xenides, D.; Vchirawongkwin, V. *Theor. Chem. Acc.*, **2006**, *15*, 77.

Ionic Liquids – Novel Solvents for Green Chemistry, Electrochemistry and Biological Chemistry

Douglas R. MacFarlane

School of Chemistry, Monash University, Clayton Victoria 3800 Australia.

Ionic liquids have recently become widely studied for a variety of applications because of the useful combination of properties that they can offer[1]. These ambient temperature liquid salts are mostly organic salts of ions that are of low symmetry and/or delocalized charge. Most examples involve aprotic cations, but a large family of "protic" ionic liquids is also known which contain an exchangeable proton. Recent discoveries have produced examples that are sufficiently fluid at room temperature to be useful as solvents in chemical operations, including synthesis and various product extraction situations. The intrinsic ion conductivity of ionic liquids makes them ideal as electrolytes in a variety of electrochemical applications and devices such as photoelectrochemical solar cells and lithium batteries. However, not nearly enough is known yet about the physical, thermodynamic and transport properties of these liquids and much more work is needed in these areas.[2]

This talk will overview the field of ionic liquids and present a number of examples of their use as solvents drawn from a range of fields.

[1] Forsyth, S.A.; Pringle, J.M.; MacFarlane, D.R. *Aust. J. Chem.*, **2004**, *57*, 113.
[2] MacFarlane, D.R.; Seddon, K.R. *Aust. J. Chem.*, **2007**, *60*, 3.

Ionic Liquids: Are they Salts or High Boiling Organic Liquids?

Kenneth N. Marsh

Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand.

It has been widely believed that ionic liquids were molten salts with no measurable vapour pressure. Recent work indicates that many ionic liquids are distillable at 470 K with no significant decomposition. The mechanism for this transfer from the liquid to vapour remains unresolved. Hence it is appropriate to ask "what thermophysical properties of should be used to classify materials as a salt". Such properties can include vapour pressure, the electrical conductivity of the liquid salt, the electrical conductivity of the salt at low dilution in a polar solvent such as water or ethanol, and the zero frequency relative permittivity. In addition properties of mixtures of ionic liquids with organic compounds, such as vapour-liquid equilibria, liquid-liquid equilibria, excess enthalpies, and excess volumes can give a clue as to the nature of ionic liquids. Theoretical calculations based on *ab-initio* methods can also give a guide as to whether ionic liquids exist primarily as ions or as associated ion pairs in the pure liquid state and in mixtures with organic liquids.

Interpretations of the measurements of the above properties for ionic liquids as well as the theoretical calculations will be reviewed.

Ultrafast Proton Transfer in Aqueous Acid-Base Neutralization

Erik T.J. Nibbering,[a]* Omar F. Mohammed,[a] Dina Pines [a] and Ehud Pines [a]

[a] *Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D–12489 Berlin, Germany;*
[b] *Department of Chemistry, Ben Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84125, Israel. E-mail: nibberin@mbi-berlin.de ; URL: http://staff.mbi-berlin.de/nibberin/ and http://www.mbi-berlin.de/en/research/projects/2-04/index.html.*

Modern discussions of acid-base reactions have evolved from the seminal studies of Eigen and Weller[1,2]. The general kinetic approach for acid-base reactions in aqueous solutions consists of three reaction branches[2]: (a) direct proton exchange between acid and base, (b) acid dissociation to solvent followed by proton scavenging by the base, and (c) water hydrolysis by the base followed by the neutralization reaction of the acid by the hydroxyl anion. Judging by the magnitude of the reaction radius in typical (diffusion-controlled) acid-base reactions it has been estimated that up to 2 – 3 water molecules separate when acid and base exchange a proton through pathway (a) [1]. In reality, however, this value is likely to be an averaged value of several encounter complexes (with *n* rearrangements steps) leading to proton transfer.

Photoacids can be used as a means to follow proton transfer dynamics to a neutralising base in real time by photoinitiation. The outcome of the observed dynamics, i.e. the reaction rates and yields depend on the relative strengths and concentrations of acid and base. We have investigated the aqueous neutralization reaction of the photoacid pyranine and carboxylate bases ($^{-}OOCCH_{3-x}Cl_x$) ($x = 0 - 3$) with femtosecond infrared spectroscopy[3]. Here we are able to dictate the outcome of the reaction dynamics by tuning the number of chlorine atoms x. We have identified two innermost types of encounter complexes (tight and loose), resulting in a sub-150 fs proton dissociation lifetime of the photoacid[4–6]. The proton transfer in both encounter complexes is found to be reversible. The step-wise, von-Grotthuss type[5–6], proton transfer in loose complexes involves a first step leading to a H_3O^+ like cation resembling the proton solvation core in the Eigen cation, $H_9O_4^+$, and a second and final transfer to the base on much slower picosecond time scales. The stability of the hydrated proton in the loose complex increases with decreasing reactivity (basicity) of the carboxylate base as measured in bulk water. We have applied a unified reaction dynamics model in which we have approximated all possible configurations between acid and base by tight ($n = 0$), loose ($n = 1$) and solvent switch ($n > 1$) complexes, as well as acid and base fully separated by the solvent. Whereas the fully separated acid and base first have to diffuse, all other complexes are connected to each other through reversible proton transfer steps. Step-wise proton shuttling through water provides a route for proton transfer which circumvents further desolvating the acidic and basic groups necessary for direct transfer.

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Structural Characterization of Supramolecular Architectures in Solution

Gábor Pálinkás

Chemical Research Center, Hungarian Academy of Sciences, Budapest, 1525 Hungary.

Several spectroscopic and diffraction methods have been employed to determine the coordination numbers and solvation shells of molecules and ions in solution. Coordination numbers, distances between atoms, and temperature factors of the atom pairs have been determined from the intensities of elastically scattered electrons, photons, and neutrons. Aqueous or alcoholic solutions, their mixtures and ion pairing have been examined by wide-angle X-ray diffraction. Currently, X-ray and neutron diffraction methods are being utilized to examine liquids and solutions under high pressure and temperature, complexes with complicated structures that are insoluble in water, and even supramolecular assemblies.

Molecular self-assembly: the process whereby molecules spontaneously form ordered supramolecular ensembles via noncovalent interactions, is an area of considerable current interest and research activity due to its broad impact across a wide range of materials and biomimetic chemistry. A major challenge in supramolecular chemistry and self-assembly, is proper structural characterization. Mass spectrometry and multinuclear NMR spectroscopy are most commonly employed to provide proof of composition and to deduce structural information, respectively. In cases where a suitable single crystal can be obtained, classical single-crystal X-ray diffraction provides the most reliable structural data, but only in the solid state. An important question in the area of supramolecular chemistry and self-assembly is the formation, shape, and structure of these species in the solution. Multinuclear NMR, by exploiting the nuclear Overhauser effect (NOE), provides support for the existence of shape-persistent supramolecular macrocycles and three-dimensional cages. The ability to deduce structure from scattering data is determined to a large extent by the complexity of the molecular system. For large supramolecular assemblies such as proteins and micelles, solution wide-angle scattering features are diffuse and contain overlapping contributions from many structural elements. However, clear opportunities exist for structural characterization of self assemblies in solution using also traditional high-angle X-ray scattering because such molecular aggregates often have structural complexities that are intermediate between those of proteins and small molecules.

In this presentation I wish to demonstrate the state of the art using a combination of different methods to determine the structure as well as the shape and size of self-assembled supramolecular species in solution phase.

Interaction of Fluids with Surfaces and Nanoparticles

Nicholas Quirke

Computational, Theoretical and Structural Chemistry, Imperial College, London, UK.

The way fluids flow into and fill nanopores is of interest to physicists, chemists, engineers and biologists. It is of particular concern to those developing nanofluidic devices. Nanoscale flow is dominated by surface properties and these can be studied directly using molecular simulation of model systems. Such simulations describe equilibrium states, steady states and transient flow regimes.

In this lecture we review key results concerning the interaction of fluids with carbon nanopores from theory, simulation and experiment, and present new results for dynamical properties of nanomaterials in aqueous solutions. We review the prospects for carbon based nanofluidic technolgy.

See for example:

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Combining Surface Nonlinear Spectroscopy and Molecular Dynamics Simulations to Understand Molecular and Ionic Interactions at Liquid-Liquid Interfaces.

Geraldine L. Richmond

Department of Chemistry, University of Oregon, Eugene, OR, USA.

This presentation will highlight our most recent results in which we explore the structure and bonding that occurs at the interface between water and a series of hydrophobic organic liquids of differing molecular structure and polarity. Our approach combines vibrational sum frequency spectroscopy to measure the vibrational spectrum of interfacial molecules, with theoretical calculations of corresponding VSF spectra acquired by employing molecular dynamics simulations and molecular hyperpolarizability calculations. The direct comparison of our experimental and theoretical results gives new information about interfacial population densities, bonding character and orientation of both aqueous and organic interfacial molecules. Other insights to be discussed derived from these studies include the general nature of water adjacent to hydrophobic surfaces, similarities of some systems with water behavior at air/water interfaces, ions at liquid/liquid interfaces, and water and ion penetration into the organic phase.

Molecular Dynamics Simulation Studies of Ionic Liquids

Grant D. Smith*, Oleg Borodin and Liyong Chen

Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah, USA.

Atomistic molecular dynamics (MD) simulations have played an important role in our understanding of complex fluids. Our group has employed atomistic MD simulations methods utilizing carefully parameterized, quantum chemistry based potentials in the study of numerous water- and polymer-based solutions, including self-assembling polymer solutions, electrolyte solutions, colloidal suspension and nanoparticle suspensions. Recently we have extended these methods to solutions based upon ionic liquid solvents. I will discuss insight into the structure, dynamics and transport properties gleaned from our recent and ongoing MD simulation studies of simple ionic liquids, ionic liquids that self assemble on the nanometer length scale, ionic liquids doped with lithium salts and ionic liquid/liquid crystal membranes.

Polyelectrolyte Hydration: Theory and Experiment

V. Vlachy[a]* and Yu V. Kalyuzhnyi[b]

[a] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1001 Ljubljana, Slovenia;*
[b] *Institute for Condensed Matter Physics, Lviv, Ukraine.*

Properties of polyelectrolytes differ from those of low–molecular electrolytes as also from neutral polymers. In addition to the long–range Coulomb interaction, the water mediated ion–specific forces can be important. These effects are crucial for understanding the processes involving biological polyelectrolytes as also industrial applications. Examples showing importance of the ion–specific interaction are given in Refs. [1,2]; the enthalpies of dilution ΔH of polyelectrolyte solutions were found to be either negative or positive, depending on the nature of counterion, temperature, and the charged group on a polyion. The classical model[1–3], treating solvent as dielectric continuum, polyion as charged hard cylinder and ions as charged hard spheres, predicts for ΔH to be always negative.

In the present study a theory based on an extension of the product reactant Ornstein–Zernike theory[4,5] was applied to model polyelectrolyte solution. Solvent molecules were modeled with four square–well sites so they can coordinate with each other and charges in the solution. Flexible polyions with 120 monomer units and equivalent number of oppositely charged counterions were present in the system[6]. The strength of the water–counterion interaction was varied, while the water–polyion and water–water interactions were constant. Note that in this model the "water" molecules had no charges; dielectric constant of the solution was assumed to be equal to that of pure water under these conditions. Thus, the pair potential for the present model was written as a sum of the hard–sphere term, Coulomb term, and the term describing association. Despite of its simplicity the model was able to explain basic experimental results of real polyelectrolytes[6]. For strongly hydrated counterions we obtained $\Delta H < 0$, i.e. the heat is released in the process of dilution. For weakly hydrated counterions (or at low temperature) we observed an opposite effect, heat is consumed in dilution. The results were consistent with experimental data[1,2]; for example, endothermic effect was observed in case of dilution of 3–3 ionenes with bromine and chlorine counterions, while exothermic effect was measured in solutions where fluorine counterions were present.[2] The osmotic coefficients, calculated by this approach, were in qualitative agreement with experimental data and consistent with the ΔH results.

These results will be complemented with the all–atom explicit water Molecular Dynamics simulations for short 3–3 ionenes with bromine and chlorine counterions, and measurements of the dielectric relaxation for 3–3, 4–5, and 6–9 ionene solutions with various F^-, Cl^- and Br^- counterions, now conducting in collaboration with our co–workers in Lviv and Regensburg.

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The Synthesis and Stability of Wroewolfeite, $Cu_4SO_4(OH)_6.2H_2O$

Timothy R. Dabinett, David Humberstone, Peter Leverett and Peter A. Williams*

School of Natural Sciences, University of Western Sydney, Locked Bag 1797, Penrith South DC NSW 1797, Australia.

An astonishing range of compounds in the system $CuO–SO_3–H_2O$ exists and most can be synthesized at temperatures ranging from 0 to 50°C. Naturally occurring species precipitated from aqueous solution are spertiniite, $Cu(OH)_2$, which can be dehydrated to tenorite, CuO, antlerite, $Cu_3SO_4(OH)_4$, brochantite, $Cu_4SO_4(OH)_6$, posnjakite, $Cu_4SO_4(OH)_6·H_2O$, langite and wroewolfeite, $Cu_4SO_4(OH)_6·2H_2O$, and redgillite, $Cu_6SO_4(OH)_{10}·H_2O$. The latter is extremely rare. Some of these phases have in the past been important ore minerals of copper. Current interest in their chemistry stems in part from their environmental significance, including their presence in acid mine drainage trains and their role in the removal of copper from waste waters. Titration of aqueous copper(II) sulfate solutions with aqueous NaOH at temperatures ranging from 0 to 25 °C results in a complex Ostwald Step Rule cascade of basic copper sulfate phases. At 25 °C the thermodynamically stable phase is brochantite, but posnjakite is obtained initially. At lower temperatures, but above 0 °C, wroewolfeite forms first. If left in contact with the reaction solution, wroewolfeite converts to posnjakite and brochantite in turn. However, at 0 °C synthetic wroewolfeite is stable for periods longer than a week, even in contact with the reaction solution, and a stability constant for it has been obtained. For the reaction below, $\lg K = -16.3(1)$ at

$$0.25Cu_4SO_4(OH)_6·2H_2O(s,\text{wroewolfeite}) \rightleftharpoons Cu^{2+}(aq) + 0.25SO_4^{2-}(aq) + 1.5OH^-(aq) + 0.5H_2O(l)$$

0 °C and $I = 0$, as determined by solution methods. Stability relations between minerals of stoichiometry $Cu_4SO_4(OH)_6·nH_2O$ ($n = 0, 1, 2$) are complex and governed by a combination of thermodynamic and kinetic influences, some of which remain to be elucidated. High concentrations of Mg^{2+} ions (1 M) prevent the isolation of wroewolfeite at any temperature down to 0 °C, but substitution of foreign ions in the lattices appears to have no bearing upon stabilities of the various basic Cu(II) sulfates. No syntheses are available for redgillite or langite, both of which appear to owe their existence to rates of nucleation that will ultimately depend on the intricacies of solution speciation.

On the Role of Solvent Environment in Alcohol-induced α-Helix Formation of Model Peptides

Toshio Yamaguchi,[a]* Takeharu Fujinaga,[a] Satoshi Nakamura,[a] Sergey Krishtal,[a]
Koji Yoshida,[a] Sannamu Lee,[a] Kenji Kanazawa [b] and Tadashi Nemoto [b]

[a] *Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814–0180, Japan;*
[b] *Biological Information Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, 305–8567, Japan.*

It has recently been found that alcohol-water mixtures undergo structure transition from tetrahedral-like water network to zigzag chain-like alcohol structure at specific alcohol concentrations with increasing concentration of amphiphilic alcohols.[1–4] It has also been found that a structural transition of peptides and proteins takes place from the random coil conformation to a helical state in alcohol-water mixtures.[5] Although alcohol-induced protein folding has been studied for a long time, the underlying mechanism has not yet been fully understood at the molecular level.

In the present study, the role of solvent environment in alcohol-induced α-helix formation of model peptides is discussed in view of the structure of aqueous solutions of alcohols: methanol (MeOH), ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The model peptides consist of 10 and 17 amino-acid residues (GLRDFIEKFK and KGRTFRNEKELRDFIEK) fragments of 28 amino-acid residues, Full Sequence Design-1 (PDB ID:1FSD). From CD results on the alcohol concentration dependence of molar ellipticity values at 222 nm in α-helix formation of the peptides, it has been found that the order of α-helix formation is consistent with that of solvent structural transition (HFIP>TFE>EtOH>MeOH); the result suggests that the α-helix formation of the peptides is strongly associated with a solvent clusters.

Furthermore, Replica Exchange MD (REMD) simulations and 2D-NMR measurements were performed for the 10 residues fragment in ethanol-water mixtures at $x = 0.1, 0.2, 0.3, 0.4$ and 1.0, and the details of solvation structure around the 10 residues fragment were revealed in the process of structure transition. The underlying mechanism in alcohol-induced α-helix formation of the model peptide is discussed at the molecular level.

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ORAL PRESENTATIONS

(Presenters listed in alphabetical order)

Abbrvn	Session	Venue	Date	Time
TS1	Theory & Simulation – 1	ECL2	Monday	11:00 – 12:40
CS1	Chemical Speciation – 1	ECL4	Monday	11:00 – 12:40
NS1	Nanoparticles & Surfaces – 1	ECL2	Monday	14:00 – 15:40
TK1	Thermodynamics & Kinetics – 1	ECL4	Monday	14:00 –17:10
IL1	Ionic Liquids – 1	ECL2	Tuesday	10:00 –12:50
CS2	Chemical Speciation – 2	ECL4	Tuesday	10:00 –12:50
TK2	Thermodynamics & Kinetics – 2	ECL2	Wednesday	9:30 –12:00
TS2	Theory & Simulation – 2	ECL4	Wednesday	9:30 –11:20
NS2	Nanoparticles & Surfaces – 2	ECL2	Thursday	10:00 –12:30
SS1	Solution Structure – 1	ECL4	Thursday	10:00 –12:50
OS	Ohtaki Symposium	ECL2	Thursday	14:00 –16:50
IL2	Ionic Liquids – 2	ECL2	Friday	10:00 –12:50
TK3	Thermodynamics & Kinetics – 3	ECL4	Friday	10:00 –12:50

CS2

Use of Strong Iron Chelating Agents in Extraction of Iron Compounds from Archaeological Wood

Gunnar Almkvist* and Ingmar Persson

Department of Chemistry, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Degradation processes related to the presence iron compounds and high acidity in the wood of the Swedish warship *Vasa* has been reported. One hypothesis is that the oxidation of the wood polymers and sulfur compounds are catalyzed by the large amounts of diverse iron compounds present in the wood. It is therefore of interest to develop a method to extract the iron compounds, and simultaneously neutralize the acids. The iron compounds could be extracted from wood by an aqueous solution of ethylenediimino-bis(2-hydroxy-4-methyl-phenyl)acetic acid (EDDHMA) or diethylenetriamine-pentaacetic acid (DTPA) at alkaline pH, leaving only small amounts of iron compounds.[1] The extraction rate is enhanced by stirring and by higher concentration of the chelating agent. However, diffusion of compounds through the wood is the most important factor for the over-all extraction efficiency. Extraction of iron compounds deep inside the wood is time-consuming and may take years. The results from this study imply that aqueous extraction with extraordinary chelating agents at relatively high pH, 9 – 11, effectively removes iron compounds and neutralizes present acids. The results are promising and may be seen as one step towards a method used in practice in the field of conservation of iron containing archaeological wood.

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NS2

Thermodynamics of Micellization of Non-Ionic and Ionic Surfactants and Their Structural Properties in Aqueous Solution

Marija Bešter-Rogač,* Jurij Lah, Tine Martin Perger and Gorazd Vesnaver

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, 1000 Ljubljana, Slovenia.

The understanding of the micellization processes at the molecular level has a direct relevance for biological self-assembly, folding and association processes. As such it requires a complete characterization of the micellization thermodynamics including its correlation with the corresponding structural features. In this context micellization of a series of model non-ionic surfactants has been investigated recently[1].

In this work we extended the research to the model ionic surfactants (alkyltrimethylammonium chlorides) in aqueous solutions. Besides by the hydrophobic effect, the micellization of ionic surfactants in aqueous solutions is largely influenced by the mutual electrostatic interactions between the ionized head-groups and their interactions with the surrounding counterions and water molecules. Therefore, the effective charge of micelles and the nature of counterions have a significant effect on the values of thermodynamic parameters of micellization.

We have determined the temperature dependence of critical micelle concentration and the degree of micelle ionization of decyl-, dodecyl- and tetradecyltrimethylammonium chloride by means of electric conductivity measurements. The corresponding thermodynamic parameters of micellization (Gibbs free energy, $\Delta_{mic}G^{o}$; enthalpy, $\Delta_{mic}H^{o}$; entropy, $\Delta_{mic}S$,; heat capacity $\Delta_{mic}c_p^{o}$) were estimated using the pseudo-phase separation model[2,3] and compared with the corresponding values obtained directly by isothermal titration calorimetry.

To correlate thermodynamics of micellization to the micelle structure in the solution the changes in the solvent accessible surface upon micelle formation were estimated and compared with the micellar shape and size estimated by small angle X-ray scattering. In addition, the thermodynamic parameters and structural properties are discussed in terms of the alkyl chain length and the nature of the counterions.

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IL1

Solvation and Complexation of Lathanides and Actinides in Ionic Liquids: Fundamental Aspects and Possible Application for the Nuclear Fuel Cycle

Isabelle Billard,[a]* Clotilde Gaillard,[a] Ali Ouadi,[a] Emilie Jobin [a] and Silvia Stumpf [b]

[a] *IPHC, DRS, Chimie Nucléaire, 23 rue du Loess, 67037 Strasbourg, France;*
[b] *Institute for Trans-Uranium Elements (ITU), Karlsruhe, Germany.*

In many areas of chemistry, such as organic synthesis or catalysis, ionic liquids (ILs) have gained the status of potential "green" solvents of interest in view of a renewal of chemistry, from fundamental aspects to industrial applications. In the field of nuclear waste processes however, the lack of a comprehensive knowledge of their solvation properties towards lanthanides (Ln) and actinides (An) has yet hampered the development of applied studies.

Our group has started a study of the fundamental aspects of An and Ln solvation and complexation in ILs. Such a fundamental understanding is a prerequisite for the elucidation of the extraction mechanism at work in ILs, when well-known extracting moieties such as TBP (n-tri-butylphosphate) are diluted in common ILs (i.e. 1-methyl-3-butyl-imidazolium$^+$, $(CF_3SO_2)_2N^-$, BumimTf$_2$N). This knowledge will be of decisive importance in order to understand the extraction mechanism occuring when various Task-Specific Ionic Liquids (TSILs) recently synthesized in our laboratory are used instead.

The solvation sphere of Eu(III), U(VI), Am(III) and Cm(III) in various ILs has been investigated by use of UV–vis, Time-Resolved Fluorescence and EXAFS spectroscopies. The experimental data give a clear image of the solvation sphere of the various metallic cations and some insight into the competitive complexation processes occuring between the IL counter-anion (such as PF_6^-, BF_4^-, $CF_3SO_3^-$ or $(CF_3SO_2)_2N^-$) and ligands such as Cl^- or NO_3^-.[1] Our latest results on the determination of the equilibrium constant of UO_2^{2+} with NO_3^- in BumimTf$_2$N will be discussed. The differences and similarities between U(VI) or Am(III) extraction from acidified (HNO_3) aqueous solutions towards either BumimTf$_2$N/TBP or various TSIL[2] will then be presented and discussed.

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CS2

Ion Association Effects on the Experimentally Observed Dissociation Constant of Ammonium Ion

Silvia B. Black,[a,b]* Gamini Senanayake [a] and Michael Nicol [a]

[a] *Extractive Metallurgy, Division of Science and Engineering, Murdoch University, Murdoch, WA 6150, Australia;*
[b] *A.J. Parker Cooperative Research Centre for Hydrometallurgy, Murdoch University, Murdoch, WA 6150, Australia.*

Ion association was found to significantly affect the experimentally observed dissociation constant of the ammonium ion in solutions containing sodium sulfate and sodium thiosulfate, thus influencing the free ammonia concentration in solution. This study encompassed solutions containing sodium sulfate, chloride, nitrate, thiosulfate and perchlorate at an ionic strength of 3.0 and 25 °C. Experimental as well as calculated values of the dissociation constant will be presented. The importance of using the correct dissociation constant in thermodynamic studies that involve ammonia in order to obtain precise stability constants will be demonstrated in a case study.

TS1

Hydrogen Bond Dynamics in Aqueous Solutions and Vibrational Spectral Diffusion

Amalendu Chandra

Department of Chemistry, Indian Institute of Technology, Kanpur, India 208016
(E-mail: amalen@iitk.ac.in)

The hydrogen bond dynamics in pure water and aqueous solutions containing charged solutes are investigated by means of classical and *ab initio* molecular dynamics[1] simulations. The time dependent changes of vibrational frequencies of OH stretch modes of water due to hydrogen bond fluctuations are also calculated for water molecules in bulk and also in ion solvation shells. The frequency fluctuations are subsequently used to calculate spectral diffusion and frequency correlation functions to connect the kinetics of hydrogen bond fluctuations[2] to ultrafast vibrational spectroscopy[3]. Some preliminary results are also presented for hydrogen bond and frequency fluctuation dynamics and power spectra of water at interfaces and in cluster phases[4].

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IL1

Thermodynamic Phase Behavior of Ionic Liquids

Urszula Domańska-Żelazna

Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland.

The (solid + liquid), SLE and (liquid + liquid), LLE phase equilibria of ionic liquids (ILs) basing on alkyl-(2-hydroxyethyl)-dimethyl-ammonium cation [C_n] and different anions [Br^-, or $N(CN)_2^-$, or PF_6^-, or BF_4^-, or $N(CF_3SO_2)_2^-$]^{1,2} and 1-alkoxymethyl-3-methyl-imidazolium, ([$C_nH_{2n+1}OCH_2$mim]) or 1,3-dialkoxymethyl-imidazolium ([($C_nH_{2n+1}OCH_2)_2$im]) cations with different anions {BF_4^-, $N(CF_3SO_2)_2^-$}^{3,4} have been measured. The determination of the IL–solvent interaction of these salts and 1-alkyl-3-methylimidazolium cations with {[$CH_3SO_4^-$], or [$OcSO_4^-$], or [$MDEGSO_4^-$], or [TOS^-]}$^{5-7}$ anions via the solubility measurements, or excess molar volumes^8 or activity coefficients at infinite dilution measurements have been performed. The influence of high pressure up to 600MPa on IL's SLE has been also investigated. These salts mainly exhibit simple eutectic systems with immiscibility in the liquid phase with upper critical solution temperatures (UCST), not only in aromatic hydrocarbons, cycloalkanes and *n*-alkanes but also in ethers, ketones and alcohols.

The (solid + liquid) phase equilibria or (liquid + liquid) phase equilibria curves were correlated by means of the different G^{Ex} models utilizing parameters derived from the SLE or LLE. The root-mean-square deviations of the solubility temperatures for all calculated data depend on the particular system and the equation used. The (liquid + liquid) phase equilibria was predicted for many systems with COSMO–RS model.

Due to the fascinating physico-chemical properties of these ionic liquids, they seem to be significant in development of new technologies.

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TS1

Dynamics of Ions in Concentrated Electrolyte Solutions

J.-F. Dufrêche,[a]* O. Bernard[a] and B. Bagchi[b]

[a] Laboratoire Liquides Ioniques et Interfaces Chargées UMR CNRS 7612 Université Pierre et Marie Curie BC 51 4 place Jussieu 75252 Paris Cedex 05 France;
[b] SSCU Indian Institute of Science Bangalore, India–5600012.

Since the pioneering works of Debye, Hückel and Onsager, transport of ions is studied with great activity. These classical theories, based on continuous solvent models, are valid only for dilute solutions (typically less than 0.01 mol/L for the best cases). Yet, the development of important domains in recent years, such as colloidal science, electrochemistry, molecular biology or geophysics, makes necessary to propose a modern theory of transport for concentrated solutions. We will present such an approach which is able to describe the various equilibrium and transport properties of ions for aqueous concentrated solutions, by emphasizing the possible various applications.

More precisely:

- First, we will focus on the case of bulk electrolyte solutions, from a Smoluchowski approach, which predicts the various transport coefficients for concentrated solutions. The coupling between the hydrodynamic interactions (electrophoretic effect) and the electrostatic relaxation together with their time-dependence (which can be measured from dielectric spectroscopy experiments) will be explicited. Mode-coupling theory (MCT) explain the discrepancy between the short-time (QENS) and long-time measurements.

- Second, we will deal with confined electrolyte solutions. In that case, the bulk descriptions are not valid, since the mobility of the ion is modified by the confinement. We will explain how to model these systems rigorously, the confinement effect being described by effective (solvent-averaged) parameters which can be obtained from Molecular dynamics (microscopic simulations). Several applications for clays and colloidal solutions will be proposed.

It is worth noting that these theories are in agreement with experiments and simulations up to concentrated solutions (1 – 2 mol/L). They are examples of so-called "coarse-graining" procedures where we first average over the solvent degrees of freedom in order to obtain a simple but rigorous description for the ions. As a matter of fact, they are no adjustable parameters, since all of them can be obtained from Molecular dynamics simulation. In the case of bulk solutions, the use of the Mean Spherical Approximation (MSA) allows simple explicit solutions to be obtained, which is very important for practical use.

CS2

NOM and Trace Element Speciation Modelling: a Road Paved with Good Intentions and few Useful Results

Montserrat Filella

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Quai Ernest-Ansermet 30, CH–1211 Geneva 4, Switzerland.

There is a general consensus that Natural Organic Matter (NOM) plays a key role in the speciation and fate of trace elements in natural waters. However, the inclusion of the corresponding equilibria in speciation codes has proved elusive over the last 40 years. With the aim of clarifying the situation, the following aspects will be discussed in this communication:

1- How NOM-trace element interactions are taken into account in existing codes: the realm of 'best' models and hidden fitting.

2- How existing codes are actually used in 'real life' (survey of papers published in well-known applied journals): the deceiving reality.

3- Why laboratory results can seldom be used in 'real life': the forgotten facts (e.g., "not all elements are copper", "not all NOM are humics", the inconstant constants).

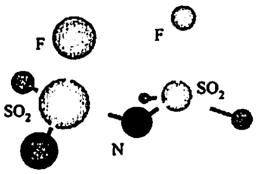
4- Alternatives.

IL2

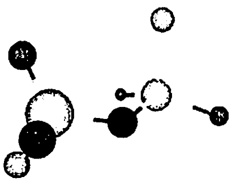
Conformational Equilibrium of Bis(fluoroslufonyl) Imide Anion in Room-Temperature Ionic Liquid

K. Fujii,[a*] S. Seki,[b] Y. Umebayashi [c] and S. Ishiguro [c]

[a] *Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga Univ., Honjyo-machi, Saga 840–8502, Japan;*
[b] *Materials Science Research Laboratory, Central Research Institute of Electric Power Industry, Komae, Tokyo 201–8511, Japan;*
[c] *Department of Chemistry, Faculty of Science, Kyushu Univ., Hakozaki, Higashi-ku, Fukuoka 812–8581, Japan.*



FSI$^-$ C_1 conformer



FSI$^-$ C_2 conformer

Bis(trifluoromethanesulfonyl) imide anion (TFSI) with imidazolium based cations such as 1-ethyl-3-methyllimidazolium (EMI$^+$) is one of the most popular room-temperature ionic liquids (RTILs). It has been established in our previous work that the TFSI consists of two conformers of C_1 and C_2 symmetry in the ionic liquid. Bis(fluoroslufonyl) imide anion (FSI) which is substituted CF$_3$ group of TFSI by F, gives a low viscosity RTIL (EMI$^+$FSI : 18 mPa·s, EMI$^+$TFSI : 33 mPa·s).[1] Structure of FSI anion in ionic liquid EMI$^+$FSI was studied by Raman spectroscopy and DFT calculations. Raman spectra of EMI$^+$FSI in the range of 280 – 400 cm^{-1} showed the relatively strong bands at 293, 328 and 360 cm^{-1} and the shoulder bands at 305, 320 and 353 cm^{-1}. These bands are ascribed to FSI because of no significant bands for EMI$^+$ in this frequency range. The strong bands for FSI appreciably decreases with increasing temperature, whereas the shoulder slightly increases, suggesting that a conformational equilibrium is established in the liquid state, as well as TFSI. DFT calculations predicted that FSI has the two conformers of C_2 and C_1 symmetry, global and local minima, respectively, with an energy difference 4 kJ mol^{-1}. From theoretical Raman bands obtained by full geometry optimizations followed by normal frequency analyses, it is found that the observed 293, 328 and 360 cm^{-1} bands correspond to the C_2 conformer and the 305, 320 and 353 cm^{-1} bands (shoulder) to C_1 one. The observed Raman band were deconvoluted to extract intrinsic bands of FSI, and the conformational enthalpy from C_2 to C_1 was evaluated to be 3.1(1) kJ mol^{-1}. The enthalpy value is in good agreement with that obtained by theoretical calculations and is almost similar to the corresponding value of TFSI (3.5 kJ mol^{-1}).

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IL1

Thermodynamics of Ionic Liquids

Leslie Glasser

Nanochemistry Research Institute, Curtin University of Technology, Perth WA, 6845, Australia.

Ionic liquids are of increasing interest, at least partly because of their low environmental impact in synthesis and application, and so their physical properties need to be understood. There may, in principle, be up to 10^{18} salts forming ionic liquids so that predictive thermodynamic methods[1,2] are essential in order to guide practitioners in their use.

This paper reports on the current state of methods for predicting properties of ionic liquids such as molar volume, viscosity, conductivity, entropy, melting point, and so forth.

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TK2

A Statistical Approach to Cation – Solvent Interactions

Gerhard Gritzner* and Michael Auinger

Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, A4040 Linz, Austria

A statistical approach for the evaluation of single-ion Gibbs energies of transfer of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, Ba^{2+}, Ag^+, Tl^+, Cu^+, Zn^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} into 40 solvents based on the spectral theorem is presented. It is shown that the Gibbs energies of transfer depend both on the nature of the cation and on the donor site of the respective solvent molecule. Correlation of the data for the investigated cations required separating the solvents into subgroups according to their donor atoms in the solvent molecule. Gibbs energies of transfer into oxygen donor solvents could be correlated with the Born term $[N_L (z_i e_o)^2/(8 \pi \varepsilon_o r_i)]$. Several cation parameters were investigated with respect to the transfer data into nitrogen and sulfur donor solvents. No correlations were found. Thus the use of cation parameters derived from the statistical analysis are proposed to account for the Gibbs energies of transfer into nitrogen and sulfur donor solvents.

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IL2

Transport Properties of Ionic Liquids at High Pressure

K.R. Harris [a*] and M. Kanakubo [b]

[a] *School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Australian Defence Force Academy, Canberra ACT, Australia;*
[b] *Research Center for Compact Chemical Processes, National Institute of Advanced Industrial Science and Technology, Sendai, Japan.*

We have determined the viscosities,[1-3] conductivities[4,5] and ionic self-diffusion coefficients[4] for a number of ionic liquids at high pressure. The results are analysed in terms of fractional Stokes-Einstein and Walden relationships. Ion-ion interactions are also examined using velocity correlation coefficients and the Nernst-Einstein relationship.

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[4] Kanakubo, M; Harris, K.R.; Tsuchihashi, N.; Ibuki, K.; Ueno, M. *J. Phys. Chem. B*, **2007**, *111*, 2062.
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TK1

Cooperative Effects of Spin-State Transition in Solution

Nader Hassan,[a*] Andrei B. Koudriavtsev [b] and Wolfgang Linert [a]

[a] *Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163–AC, A–1060 Vienna, Austria;*
[b] *Analytical Centre, D. Mendeleev University of Chemical Technology of Russia, Moscow 125047, Russia.*

Thermally-induced spin transitions between the low-spin and high-spin states of Fe(II)-complexes are commonly observed in the solid state generally with low transition temperatures. In this case cooperative effects are known, which lead to steep transition curves as well as hysteresis effects. These phenomena can be visualised as being due to deviations from the linearity of the respective van't Hoff plots and are usually explained in terms of solid state properties like vibrational interactions and/or by strain-stress tensor approaches.

However, spin transitions are also observed in solutions of spin-crossover complexes and in some cases deviations from linear van't Hoff plots can be observed, which can obviously not be explained in terms of solid state properties. Such an example is presented and discussed in some detail. The given analysis is based on isoequilibrium relationships[1] found for the spin-crossover of differently substituted $Fe(bzimpy)_2(ClO_4)_2$ (bzimpy = 2,6-bisbenzimidazol-2-yl)pyridine) measured in different solvents and clarifies that protonation and deprotonation can play an important role in spin-transition phenomena.[2] This sheds light on the unexpected occurrence of cooperative effects in solution.

Acknowledgements: Thanks are due to the Austrian Science Foundation for financial support of this investigation under the project FWF–19335–N17.

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TK2

Volumetric Properties of the Glycyl Group of Proteins in Aqueous Solution at High Pressures

Gavin R. Hedwig,[a]* Einar Høgseth [b] and Harald Høiland [b]

[a] *Institute of Fundamental Sciences – Chemistry, Massey University, Private Bag 11222,*
Palmerston North, New Zealand;
[b] *Department of Chemistry, University of Bergen, N–5020 Bergen, Norway.*

In recent years, there has been a growing interest in the study of proteins and protein unfolding at high pressure. In addition to the fundamental importance of understanding protein stability in the temperature-pressure plane, interest in proteins at high pressure has also arisen because of biotechnological applications and from the discovery of deep-sea organisms that are well adapted to life at high pressures.

For a quantitative assessment of pressure induced protein folding/unfolding, it is necessary to have information on the pressure dependence of the partial molar volume at infinite dilution, i.e. the partial molar isothermal compression, $K_{T,2}^{o}$ $\{K_{T,2}^{o} = -(\partial V_2^{o}/\partial p)_T\}$, for both the native and unfolded forms of the protein over a wide pressure range. The normal procedure used to determine $K_{T,2}^{o}$ at ambient pressure is to firstly obtain the partial molar isentropic compression through speed of sound and solution density measurements, then convert this into the isothermal quantity. This approach is not generally applicable at high pressures because solution density data and the various thermodynamic properties required for the isentropic to isothermal conversion are not available. In this paper, a method is described for calculating from the pressure dependence of sound speed data the partial molar volumes, isentropic and isothermal compressions of a solute at infinite dilution over a wide pressure range.

Protein hydration plays a crucial role in the structure and function of proteins in aqueous solution. The partial molar isothermal compression of a protein in aqueous solution is essentially comprised of two parts, an intrinsic contribution and a hydration term. Since proteins are large complex molecules, the study of small solutes chosen to model various functional groups of the protein can assist in the understanding of the hydration term. In previous work, we determined the partial molar isothermal compression of the backbone glycyl group, CH_2CONH, of a protein at 298.15 K and at ambient pressure. The model compounds used were the series of peptides with the amino acid sequence ala(gly)$_n$, $n = 1$–4. As an extension of this work to high pressures, we present new partial molar volumes, isentropic and isothermal compressions for the amino acid alanine and these peptides in aqueous solution at 298.15 K and at pressures over the range 5.0 to 100.0 MPa. The glycyl group contributions obtained from these results will be presented.

IL2

Analysis of Ionic Motions in Plastic Crystals by Dielectric Response

Junhua Huang,[a]* Douglas R. MacFarlane,[b] Maria Forsyth [c] and Anthony F. Hollenkamp [a]

[a] *CSIRO Energy Technology, Box 312, Clayton South, Victoria 3169, Australia;*
[b] *School of Chemistry, Monash University, Clayton, Victoria 3800, Australia;*
[c] *Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia.*

Some ionic liquids exhibit interesting plastic crystalline phases, where the ions perform rotational motion while their centres of mass occupy fixed sites in the crystalline lattice. The rotational motion of the immobile ions could facilitate the diffusional motion of the mobile ions and thus contribute to a high conductivity.[1] In this work, we study the rotational and diffusional motions of the ions in plastic crystalline phases of N,N-methyl-ethylpyrrolidinium bis(trifluoromethanesulfonyl) imide (P12TFSI) by dielectric measurements. We analysed that the dielectric response is composed of dipolar response, corresponding to the ionic rotational motion, and charge carrier's response related to the diffusional motions. The diffusional motion is believed to contribute to a higher conductivity through: i) a larger number of diffusing ions; and/or ii) a higher hopping rate. We derived the AC conductivity $\sigma(\omega)$ from the dielectric response, and further differentiated the contributions from the number and the hopping rate of ions diffusing through[2]:

$$\sigma(\omega) = \varepsilon_0 \omega \varepsilon_r''(\omega)$$

$$\sigma(\omega) = K\omega_p + K\omega_p^{1-n}\omega^n = \sigma(0) + A\omega^n$$

$$\omega_p = \left(\frac{\sigma(0)}{A}\right)^{\frac{1}{n}}$$

where $\sigma(0)$ is DC conductivity; ε_o is the electric permittivity of free space; $\varepsilon_r''(\omega)$ is dielectric loss; n is a constant in the range of 0.6 – 0.95; ω_p is the ionic hoping rate; K is related to the concentration of mobile ions. We found that, for the plastic crystalline phase at lower temperature, the increase in conductivity is mainly attributed to the increase in the ionic hopping rate, while for the higher temperature phases, ion diffusion becomes increasingly important.

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IL1

From Ionic Liquid to Electrolyte Solution – Cooperative Dynamics of Ionic Liquids Mixed with Polar Solvents

Johannes Hunger,[a]* Alexander Stoppa,[a] Glenn Hefter [b] and Richard Buchner [a]

[a] *Institut für Physikalische und Theoretische Chemie der Universität Regensburg, 93040 Regensburg, Germany;*
[b] *Chemistry Department, Murdoch University, Murdoch, WA, Australia.*

Although room temperature ionic liquids (RTILs) are becoming more common as solvents in organic synthesis, only limited information exists about their structure and their interaction with solutes. Thus, the search for new applications of these novel solvents is generally empirical. Understanding the inter-molecular interactions of RTILs and their mixtures with other compounds - be they co-solvent, impurity or product of a reaction conducted in the RTIL - is now regarded as a prerequisite for exploiting the full potential of RTILs in technical processes.

Recently, Dupont[1] reviewed the current knowledge on the structural organization of imidazolium-based ionic liquids. The available information suggests that these RTILs form an extended hydrogen–bond network in the pure liquid phase that strongly resembles the structure of the corresponding solid. This network breaks up on addition of solutes. According to Dupont's scenario, supramolecular aggregates of the constituent ions of the RTILs initially dominate. With increasing dilution of the IL first triple ions (TI), then contact ion pairs (CIP) and finally solvent separated ion pairs (SIP) should become the dominating species. However, whilst this scenario is more or less intuitive, actual evidence is still limited because many of the commonly used techniques are insensitive to the invoked features.

This contribution presents the first results from our investigation of the binary mixtures of the RTIL butylmethylimidazolium tetrafluoroborate ([bmim][BF_4]) with acetonitrile (AN), dimethylsulfoxide (DMSO) and water using dielectric relaxation spectroscopy (DRS). Due to its sensitivity to dipole fluctuations, DRS can yield information about all kinds of ion pairs and ion solvation.[2] Our results show that for all investigated [bmim][BF_4] concentrations only a single ion-pair species can be detected in water, DMSO and AN. The influence of hydrogen bonding on the solvation of [bmim][BF_4] will be discussed.

Particular consideration will be given to the question, if there is a transition from the cooperative dynamics typical for RTILs to that of "normal" electrolyte solutions. This transition is probably accompanied by the loss of many solvent properties which make RTILs interesting for technical applications and therefore is of fundamental importance.

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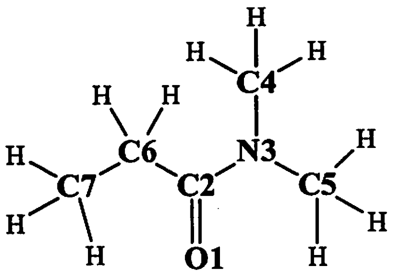
CS1

Solvation Number and Conformation of *N,N*-Dimethylacrylamide and *N,N*-Dimethylpropionamide in the Coordination Sphere of the Cobalt(II) Ion in Solution Studied by FT–IR and FT–Raman Spectroscopy

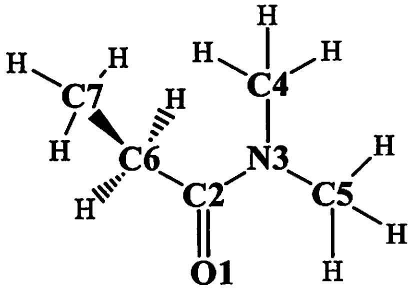
**Mitsunori Asada, Takushi Mitsugi, Takahiro Ogura, Kenta Fujii,
Yasuhiro Umebayashi and Shin-ichi Ishiguro***

*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka,
812–8581, Japan (analsscc@mbox.nc.kyushu-u.ac.jp)*

The solvation number and conformation of *N,N*-dimethylacrylamide (DMAA) in the coordination sphere of the cobalt(II) ion in solution have been studied, and compared with those of *N,N*-dimethylpropionamide (DMPA) by means of FT–Raman and FT–IR spectroscopy. Both solvents are present as either the planar *cis* or nonplanar staggered conformer in equilibrium, and the former is more stable in the bulk. As these solvents solvate the metal ion through the carbonyl O atom of the acryl (DMAA) or propionyl (DMPA) group, the solvation structure around the metal ion is highly congested to reduce the solvation number and/or to lead to the conformational geometry change of solvent. It turned out that the solvation number of the cobalt(II) ion is four for both DMAA and DMPA at 298 K, and that DMPA changes its conformation upon solvation, whereas DMAA hardly changes. The enthalpy of conformational change ΔH° for DMPA is 5 kJ mol^{-1} in the bulk, and is -9 kJ mol^{-1} in the coordination sphere of the cobalt(II) ion. On the other hand, the corresponding ΔH° value for DMAA is 9 kJ mol^{-1} in the bulk.



planar *cis* DMPA



nonplanar staggered DMPA

IL2

Acidity and Basicity of Ionic Liquids of Onium Salt

Ryo Kanzaki,* Kuniaki Uchida, Yasuhiro Umebayashi and Shin-ichi Ishiguro

Department of Chemistry, Faculty of Science, Kyushu University, 6–10–1, Hakozaki, Higashi-ku, Fukuoka, Japan, 812–8581

Room-temperature ionic liquids of onium salt are classified into an amphoteric solvent in terms of acid-base concept. In an amphoteric ionic liquids consist of Brønsted acid (HA) and base (B), the equilibrium K_{ap} = [HA][B] for $A^- + HB^+ \rightarrow HA + B$ is established, which corresponds to the autoprotolysis in amphoteric molecular liquids, for example, $K_w = [H_3O^+][OH^-]$ for $2H_2O \rightarrow H_3O^+ + OH^-$in water. In typical amphoteric ionic liquid, ethylammonium nitrate (EAN), we have determined the equilibrium constant of $K_{ap} = [EtNH_2][HNO_3]$. The values obtained are $10^{-9.83}$ by hydrogen electrode and $10^{-10.00}$ by ion-sensitive field effect transistor (ISFET) electrode at 298K. These values show that EAN involves 1.2×10^{-5} mol dm^{-3} $EtNH_2$ and HNO_3, and pH (= $-\log[HNO_3]$) = 4.9 under a neutral condition, when the ionic species ($EtNH_3^+$ and NO_3^-) is predominantly (concentration is 10^6 higher). In methylimidazolium trifluoroacetate ($MIm^+\cdot CF_3COO^-$), K_{ap} value estimated is $10^{-3.1}$ at 333K, indicating the ionic species are still predominant. However, the K_{ap} value in methylimidazolium salts of acetate and formate are larger than that of trifluoroacetate, and the neutral species significantly exists in these solvents.

In the mixture of water and EAN, we have also determined K_{ap}. The glass electrode is well available when the molar fraction of water $x_W > 0.1$. As shown in Figure 1, the value of K_{ap} increases with increasing x_W, kept almost constant at $0.1 < x_W < 0.9$, and then increases drastically at $x_W > 0.9$. The dependence of K_{ap} on x_W can be well reproduced by assuming $\kappa_A = (a_{HNO3}\cdot a_{H2O})/(a_{H3O}\cdot a_{NO3})$ and $\kappa_B = (a_{EtNH2}\cdot a_{H2O})/(a_{OH}\cdot a_{EtNH3})$. These equations have been established in the mixture of water and alcohols to explain the dependence of K_{ap} by the fraction of conjugate acid and base within the solvents, and also shown to be held in water and EAN mixture. Given values of κ_A and κ_B indicate that H_3O^+ and $EtNH_2$ dominantly act as lyonium and lyate at $0.1 < x_W < 0.9$ in the mixture, while HNO_3 increases at $x_W < 0.1$ as a lyonium and OH^- increases at $x_W > 0.9$ as a lyate.

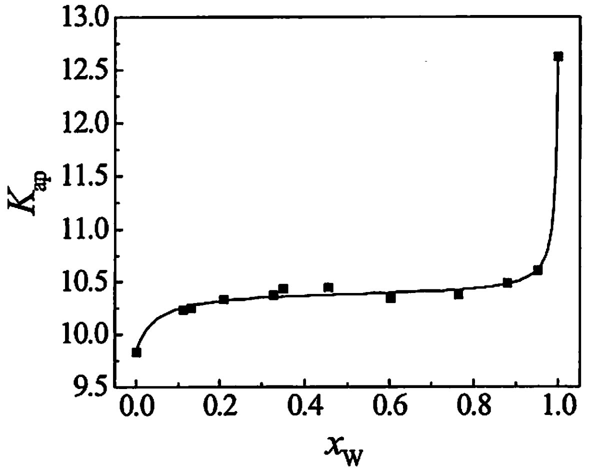


Figure 1: Dependence of K_{ap} on x_W.

TK2

Thermodynamic Process Simulation of a Bayer Refinery Circuit

Erich Königsberger

School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150, Australia

The Bayer process is employed worldwide for the refining of alumina from bauxite ores, with Australia being the world's largest producer. Although the process is mature (it was patented by the Austrian chemist Karl Josef Bayer in 1888), ongoing technological improvements are needed to increase productivity and reduce energy consumption. Insights gained from computational thermochemistry, particularly from a thermochemical simulation of the process, can help to achieve these goals.

The Gibbs energy minimiser incorporated in the thermodynamic software interface ChemApp[1] and a thermodynamically consistent, ten-component Bayer liquor model[2] were applied to a process simulation of the Bayer circuit. A FORTRAN code was specifically developed that simulates the liquor cycle from digestion, clarification, precipitation, evaporation and back to digestion, including flash cooling and heating steps. Assuming stable or metastable chemical equilibrium, this code calculates, through repetitive iterations, a steady state determined by the compositions of the input and output streams to each stage, including the associated energy balances.

The present study not only covers temperature and concentration ranges from boehmite digestion to gibbsite precipitation, it also permits exploration of boehmite precipitation as a potential energy saving modification of the process. To simulate the final step of alumina production, a counter-current reactor model describing the calcination of gibbsite or boehmite in a circulating fluid bed furnace was coded.

Furthermore, the simulation is able to predict the accumulation and precipitation of undesirable impurities in various stages of the liquor circuit. It also identifies possible reductions of the overall energy consumption of the Bayer process.

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NS2

Mixed Micelles as an Extracting Phase to Remove Metal Ions from Aqueous Environment: a Green Alternative to Liquid – Liquid Extraction

Laurence Leclercq,* Sébastien Giroux, Bernard Henry and Patrice Rubini

Groupe C2M2, Laboratoire SRSMC, Faculté des Sciences, UHP – Nancy Université,BP 239, F–54506 Vandœuvre-lès-Nancy Cedex, France.

Environnemental pollution control is becoming particularly strict nowadays, which is a further incentive to improve the removal of metal ions, generally highly toxic and carcinogenic, from aqueous streams generated by industries such as electroplating, photographic or nuclear plants. Solvent extraction is one of the conventional processes used to perform metal ions separation and extraction. However, this technique presents important drawbacks such as its requirements in volatile organic solvents, which are often toxic and flammable. That is the reason why the development of solvent-free processes might become relevant. We focus here on the use of supramolecular assemblies, such as micelles, as alternatives to traditional liquid-liquid solvent extraction. The principle of this technique is that the hydrophobic core of the micelles mimics somehow the role played by the organic phase in classical solvent extraction processes, and, thus, dissolves organic pollutants or metal ion complexes.[1] This micellar pseudophase can then be separated from the bulk by membrane processes (Micellar Enhanced Ultra Filtration, aka MEUF)[2] or thermal effects (Cloud Point Extraction, aka CPE).[3] Such processes require hydrophobic extractants able to selectively complex metal ions and to be quantitatively dissolved in the micelles. We thus developed the synthesis of biodegradable amphiphilic ligands (named C_xT, x corresponding to the length of the hydrophobic carbon chain), derivated from tartaric acid, an agricultural side product.[4]

Concerning the solubilization properties of C_8T in non ionic micelles (Triton X100, Brij 58), partitioning constants measurements have been performed and correlated with the evolution of the acid-base properties of the ligands in the presence of a micellar pseudophase. As far as complexation is concerned, C_xT are expected to complex various cations as Cu(II), Ln(III) or Pb(II), which are relevant in the field of depollution and nuclear fuel reprocessing. The complexation of Cu(II) and Pr(III) by C_3T in water have been studied.[5] The effect of the micelles on the binding constants and the structures of the complexes has been investigated and related to MEUF experiments (evolution of extraction yields with the pH, ionic strength).

The thermodynamic and structural aspects of these original extractive systems are discussed with a view to more precisely understanding the extraction process and to improving the extraction yields.

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CS2

Arsenic and Lead in the System Water – Contaminated Soils from S. Domingos Mine, Portugal

M. Clara F. Magalhães,[a]* Maria Manuela Abreu [b] and Carla Anjos [a]

[a] *Department of Chemistry and CICECO, University of Aveiro, P–3810–193 Aveiro, Portugal;*
[b] *Instituto Superior de Agronomia, Universidade Técnica de Lisboa, Tapada da Ajuda, P–1349–017 Lisboa, Portugal.*

Copper mining activities in S. Domingos mine, SE Portugal, began in the middle of the nineteenth century and lasted for more than one century, finishing forty years ago. The copper ore was also rich in arsenic and lead. To evaluate arsenic and lead dispersion, soils developed on the mine waste piles were analysed using as a reference non-contaminated soils[1] from nearby places. The soil fraction <2 mm was analysed for total concentrations of As, Cu, Fe, Mn, Pb, and Zn by INAA after acid digestion, and for the concentration of available arsenic and lead by DTPA solution extraction.

S. Domingos soils contain high levels of total arsenic (1.94 – 3.03 g As/kg soil) and total lead (4.60 – 13.4 g Pb/kg soil) but the available fractions of arsenic and lead are lower than 0.5 and 1.0 %, respectively, of the total values.

The arsenates carminite ($Fe_2Pb(AsO_4)_2(OH)_2$), mimetite ($Pb_5(AsO_4)_3Cl$), segnitite ($Fe_3Pb(AsO_4)(HAsO_4)(OH)_6$) and occasionally kankite ($FeAsO_4 \cdot 3.5H_2O$) were identified in S. Domingos soils.[1] These minerals, as well as scorodite ($FeAsO_4 \cdot 2H_2O$), can be found in soils as a result of arsenopyrite oxidation. Solubility constants are known for mimetite and scorodite. There are no values on the stability of carminite, segnitite and kankite. Nevertheless, kankite and scorodite must have similar solubilities and must be stable under similar total concentrations of arsenic and iron. Mimetite is probably the most common lead arsenate secondary mineral with a very low solubility ($\log K_s = -83.37$).[2] Iron(III) arsenates are stable in acid media with their stability being limited by the stability of iron(III) oxides. The low values obtained for available arsenic and lead show that the solid phases containing arsenic and lead, present in soils, must have a very low solubility. These results show that, under the present physical-chemical conditions, arsenic and lead in the soils of S. Domingos mine present a very low environmental risk.

In order to understand interactions between the soils and percolating rainwater, laboratory experiments have been performed, at room pressure and temperature. Soils were left in contact with water for periods of time ranging from 48 hours to 8 months, and aqueous solution and soil compositions have been studied. The experimental data will be presented and the behaviour of the system water – contaminated soil will be discussed in terms of the contribution of the arsenic containing solid phases to elemental environmental dispersion.

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CS2

Complexation of Dioxovanadium(V) and Molybdenum(VI) with NTA and IDA at Different Ionic Strengths Using SIT and Debye-Huckel Models

Kavosh Majlesi,[a*] Karim Zare [a,b] and Samira Mehnatfarsa [a]

[a] *Chemistry Department, Islamic Azad University, Science & Research,Campus, Tehran, Hesarak, Iran;*
[b] *Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran.*

Vanadium and molybdenum are widely available to biological systems, therefore the coordination chemistry of dioxovanadium(V) and molybdenum(VI) have aroused considerable interest in view of their biochemical significance. On the other hand some poly-aminocarboxylic compounds such as nitrilotriacetic acid (NTA) , iminodiacetic acid (IDA) generally called complexons are employed in many fields of application because of their strong sequestering ability towards almost all metal ions. In this research the complexation of dioxovanadium(V) and molybdenum(VI) with NTA and IDA have been studied in an ionic strength range of (0.1 to 1.0) mol dm^{-3}($NaClO_4$) at 25 °C by potentiometric and spectrophotometric techniques using Bronsted-Guggenheim-Scatchard specific ion interaction theory(SIT) and a Debye-Huckel type equation. For the Mo(VI) complex the pH was justified to 6.00 and dioxovanadium(V) complexation has been studied in the pH range 1.00 to 3.00. Debye-Huckel theory predicts the first order effects in simple electrolyte solutions. Interactions between the reacting species and the ionic medium are taken into account in the SIT model. Semi-empirical methods that have been used to model complexation reactions include the Pitzer models and SIT, and these have been shown to be equivalent for all practical purposes.[7] Therefore in this research SIT and Debye-Huckel models have been compared for the study of ionic strength effects. All of the calculations have been done on the basis of Gauss-Newton nonlinear least squares method.[1–6]

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TS2

A Statistical Associating Fluid Theory for Electrolyte Solutions

Honggang Zhao, Clare McCabe*

Department of Chemical Engineering, Vanderbilt University, Nashville TN.

The statistical associating fluid theory (SAFT)[1] has proven to be a powerful equation of state for modeling complex fluids and their mixtures. In the present work, we extended a version of the SAFT–VR equation,[2] which models non-conformal fluids with potentials of variable attractive range, to describe aqueous electrolyte solutions.[3] Water is modeled as a dipolar associating fluid following the SAFT–VR+D approach[4] in which dipolar interactions are explicitly taken into account through the use of the generalized mean spherical approximation (GMSA) to describe a reference fluid of dipolar square-well segments. Results of Monte Carlo computer simulations, performed to rigorously test the new theoretical approach before the application to real fluids, will be presented. Good agreement is obtained between the theoretical calculations and simulation data, validating the new theory. Results will also be presented for several experimental systems.

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SS1

X-ray Diffraction Characterization of Metallocyclic Complexes in Solution

Tünde Megyes,* László Kótai, Szabolcs Bálint, Tamás Grósz, Gábor Pálinkás

Institute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Budapest, P.O. Box 17, H–1525, Hungary.

Molecular self-assembly, the process whereby molecules spontaneously form ordered supramolecular ensembles via noncovalent interactions, is an area of considerable current interest and research activity due to its broad impact across a wide range of materials and biomimetic chemistry. A major challenge in all of supramolecular chemistry and self-assembly, including the metal directed approach, is proper structural characterization. An important question in the area of metal directed self-assembly is the formation, shape and structure of these species in solution. It is recognized that very weakly coordinated network solids only form in the solid state upon crystallization and do not exist as discrete species in solution, and with the development of modern electronics and high-speed computers, interest in liquid and solution structures, of molecules have steadily grown.

Recently wide-angle X-ray scattering has been used to obtain structural information on various self assembling Pt, Pd and Au containing metallacyclic complexes in solution.[1,2] The experimental structure functions for the large angle region have been analyzed and the intramolecular contributions of the metal-metal interactions are discussed. These scattering measurements provide evidence that the complexes are not as rigid in solution as they are in the single crystal. By analysis of the radial distribution functions of the solutions, direct structural information (*e.g.*, metal-metal intramolecular distances and coordination number) for the supramolecular assemblies have been determined.

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IL2

Xylanase-Hydrolyzed Reaction on Xylan in Ionic Liquids

Ika Oktavianawati,* Chunfang Zhang and Milton Hearn

ARC Special Research Centre for Green Chemistry, Monash University, VIC 3800, Australia.

Increasing concern about waste and pollution has led the pulp and paper industry to introduce environmentally safe processes such as biobleaching. However, biobleaching leads to another serious problem in the longer term: corrosion. In fact, this problem could be solved by operating at a higher temperature and reducing acid usage. Therefore, the utilization of thermophilic and alkalophilic xylanase can be anticipated to be very beneficial for the biobleaching process.

To date, there are great interests in ionic liquids, particularly as solvent in bio-catalytic reactions. One of crucial topic related with their application is on utilization of lignocellulosic materials[1]. Therefore, several ionic liquids have been employed as co-solvent in the reaction mixture for hydrolysis of xylan by xylanase. Some of the selected hydrophobic ionic liquids perform as better facilitators in the hydrolysis reaction than the hydrophilic one. Thus, the xylanase reaction profile on these ionic liquids will be further investigated.

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NS2

Charging at the Surface of Pure Oil Droplets Dispersed in Water

Toby K. Boyson [a] and Ric M. Pashley [b*]

[a] *Department of Chemistry, The Australian National University, Canberra, ACT 0200 Australia;*
[b] *Division of Research and Development, Murdoch University, WA 6150, Australia.*

Fine, micron sized, oil droplets should form a meta-stable dispersion in water, even without the use of added dispersing agents, such as surfactants and polymers.[1] This is because the surface of the oil droplets preferentially adsorb hydroxyl ions from solution and the electrostatic repulsion generated between colliding droplets is sufficient to overcome the van der Waals attraction between the droplets. Typically, the dispersions will eventually phase separate, due to buoyancy effects.[2] However, during their lifetime, these pure oil-water systems can be used to study the pristine oil/water interface and also the behaviour of a potentially ideal, colloidal solution. We have studied the charging properties of two water-insoluble oils, dodecane (DD) and bromododecane (BDD), which were dispersed in water simply by shaking de-gassed mixtures of the oil and water. The stability of the dispersions is considered under a range of solution conditions.

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OS

Structure of the Hydrated Lanthanoid(III) Ions in Aqueous Solution Determined by EXAFS Spectroscopy

Ingmar Persson,[a]* Paola D'Angelo,[b] Simone De Panfilis [c] and Magnus Sandström [d]

[a] *Department of Chemistry, Swedish University of Agricultural Sciences, P.O.Box 7015, SE–750 07 Uppsala, Sweden;*
[b] *Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale Aldo Moro 5,I–00185 Roma, Italy;*
[c] *European Synchrotron Radiation Facility, BP 220, F–38043 Grenoble Cedex, France;*
[d] *Department of Physical, Inorganic and Structural Chemistry, Stockholm University, SE–106 91 Stockholm, Sweden.*

The fifteen chemically similar elements, the lanthanum(III) ion and the lanthanoid(III) ions, have for a long time being recognized to systematically change their chemical properties. They were early divided into two subgroups, the light and the heavy lanthanoids.[1] However, the point of division is somewhat indefinite and varies depending on property chosen. Spedding and coworkers proposed 40 years ago that there is a change in the coordination number of the hydrated lanthanoid(III) ions in aqueous solution in the middle of the lanthanoid series, the so-called "gadolinium break".[2] However, any solid structural evidence for the presence of the "gadolinium break" has not been put forward so far.

In this study EXAFS data on hydrated lanthanum(III) and lanthanoid(III) ions in solid trifluoromethanesulfonate salts and in aqueous solution have been evaluated and compared. Crystallographic studies of the solid nonaaqualanthanum(III) and nonaaqualanthanoid(III) trifluoromethanesulfonates have shown that they are isostructural, forming a tricapped trigonal prism of water molecules around the central ion.[3] The EXAFS spectra of the hydrated lanthanum(III) and lanthanoid(III) ions are identical in solid state and aqueous solution showing that the solid state structures are maintained in aqueous solution, and that no change in coordination number, as proposed for the "gadolinium break", is observed. On the other hand, there is a structural change around erbium, where the number of water molecules bound to the hydrated lanthanoid(III) ions is less than nine.[3] The number of water molecules in the capping positions decreases thereafter with increasing atomic number with only 2.4 water molecules in capping positions for lutetium(III).

The structures of the hydrated lanthanum(III) and lanthanoid(III) ions in solid state and aqueous solution will presented, and the reasons behind the physical-chemical observations made for proposal of the "gadolinium break" will be discussed from a structural point of view.

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TK1

Apparent Molar Volumes and Heat Capacities of Electrolytes and Ions in N,N-dimethylformamide

Anna Płaczek,[a,b]* Glenn Hefter [a] and Wacław Grzybkowski [b]

[a] *Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia;*
[b] *Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology,*
Narutowicza 11/12, 80–952 Gdańsk, Poland.

Densities and heat capacities of numerous 1:1 electrolytes and other salts containing more highly charged ions have been measured in N,N-dimethylformamide (DMF) at low to moderate concentrations at 25 °C using a series-connected flow densimeter and Picker calorimeter system. From these data, apparent molar volumes and heat capacities have been calculated. Standard state (infinite dilution) molar volumes V_{ϕ}^{∞} and heat capacities $C_{p\phi}^{\infty}$ were obtained by extrapolation using Masson-type equations. The standard values were further split into their ionic contributions using the tetraphenylphosphonium tetraphenylborate reference electrolyte assumptions.

The salts studied included the symmetrical tetraalkylammonium (from methyl through heptyl) bromides and perchlorates as well as various series of cations and anions with a view to determining the influence of ionic size and charge on their partial molar quantities. As found in other solvents both V_{ϕ}^{∞} and $C_{p\phi}^{\infty}$ for R_4N^+ are strictly linear with respect to carbon number.

TS1

Interaction of Gold(I) and Gold(III) Ions with Nitromethane

Natcha Injan,[a,b] Michael Probst,[a]* Jumras Limtrakul,[b] Tünde Megyes,[c] Imre Bako,[c]
Tamas Radnai [c] and Szabolcs Balint [c]

[a] *Institute of Ion Physics and Applied Physics, Innsbruck University, Technikerstraße 25, 6020 Innsbruck, Austria;*
[b] *Center of Nanotechnology, Kasetsart University, Bangkok 10900, Thailand;*
[c] *Institute of Structural Chemistry, Chemical Research Centre of the Hungarian Academy of Sciences, Pusztaszeri út 59–67, H–1025 Budapest, Hungary.*

Recently, a number of new applications of gold in metallic or ionic form have appeared. In organometallic chemistry coordination- and organometallic compounds with special properties have been discovered and gold is used in sensors and microelectrodes. Applications in nanotechnology and cluster science deal with gold nanowires and the catalytic properties of gold nanoclusters. Such wires and nanoclusters are usually formed from solvated gold ions. Other potentially useful structures can also be formed by self-assembly of gold ions.

We studied the energetic and geometrical features of dimers and higher aggregates of gold(I) and gold(III) ions with nitromethane by means of quantum chemical calculations. We derived an analytical Au^+ – CH_3NO_2 potential energy expression for use in molecular dynamical simulations of gold solutions. The specific features of the nitromethane - gold interaction, of the clusters and the properties of the energy surface are discussed.

TK3

Estimation of the Vapour Pressure of Organic Compounds by a Group Contribution Method

Yash Nannoolal,[a] Jüergen Rarey,[a,b,c] Bruce Moller[a] and Deresh Ramjugernath[a*]

[a] *School of Chemical Engineering, University of Kwa-Zulu Natal, Durban 4041, RSA*
[b] *DDBST GmbH, Industriestr. 1, 26121 Oldenburg, FRG;*
[c] *Industrial Chemistry, Carl von Ossietzky University Oldenburg, 26111 Oldenburg, FRG.*

A new group contribution method for the estimation of vapour pressure data has been developed. The method is based on the structural group definitions with minor modifications of a recently published method for the normal boiling point by Nannoolal et al.[1] The results of the new method are compared to several currently-used correlative models, e.g. the Antoine equation, and have proven to be of a comparable accuracy. Correlative models give good prediction over the range of data to which they were fitted, however, extrapolation is not always so good. This new group contribution model has however been shown to extrapolate well. This method also holds the advantage over correlative models in that it can be used to predict vapour pressures even when no experimental data exist. Vapour pressure prediction requires only the molecular structure of the compound and a reference point, usually the normal boiling point. If no experimental reference point is available, the normal boiling point estimated by a method published earlier[1] can be used. The range of the method is usually from about 0.75–0.8 of the normal boiling point to the minimum of $\Delta H/R\Delta Z$ (inflection point of the vapour pressure curve in the $\ln(P^S)$ vs. $1/T$ plot). Structural groups were defined in a standardized form and fragmentation of the molecular structures was performed by an automatic procedure to eliminate any arbitrary assumptions. Currently work is been undertaken to increase the number of groups available to expand the application to more compounds.

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IL2

A New Family of Ionic Liquids Based on a New N-heterocyclic Moiety as the Cationic Component: Physico-chemical Properties and Plastic Crystal Behaviour

Thomas Ruether,* Jewel Huang, Robert J. Rees, Adam S. Best, Arek Lewandowski,
James Beavis and Anthony F. Hollenkamp

CSIRO Energy Technology, Box 312, Clayton South, Victoria 3169, Australia.

Since the introduction of 1-ethyl-3-methylimidazolium (emIm$^+$)/tetrafluoroborate (BF_4^-) and emIm$^+$/hexafluorophosphate (PF_6^-) ionic liquids by John Wilkes in 1992 and Joan Fuller in 1994 respectively, these materials, which are generally air and relatively water stable, have found an increasing variety of applications. Despite the synthesis and experimental characterization of many simular ionic liquids, our understanding of the influence of individual and mutual ion structure on the physicochemical properties of these systems is in its infancy. Here we present a study of the behaviour of a new class of ionic liquids, as a function of systematic modification of the chemical structure of the cation, while retaining the same anion bis(trifluoromethanesulfonyl)imidide (TFSI$^-$). The experimental results presented include: thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), impedance spectroscopy, viscosity, and cyclic voltammetry (CV) data. For at least one member of the family, organic ionic plastic crystal (OIPC) behaviour was established using DSC. This study demonstrates that different steric effects result from systematic structural changes of the N-heterocyclic cations and, like the imidazolium, pyrrolidinium, and piperidinium cation based systems, produce strong variation in the subsequent molten salt properties.

OS

Sulfur X-ray Absorption and Vibrational Spectroscopy of Sulfite, Sulfur dioxide and Sulfonate Solutions, and of Substituted Sulfonates $X_3CSO_3^-$ (X = H, Cl, F)

Magnus Sandström,[a]* Emiliana Damian Risberg,[a] János Mink,[b]
Lars G.M. Pettersson [c] and Mikhail Yu Skripkin [d]

[a] *Department of Physical, Inorganic and Structural Chemistry, Stockholm University,*
[b] *Department of Physics, Stockholm University, SE–106 91 Stockholm, Sweden;*
[c] *Institute of Structural Chemistry, Chemical Research Centre of the Hungarian Academy of Sciences, P.O. Box 17, H–1525 Budapest, Hungary;*
[d] *Department of Chemistry, Saint-Petersburg State University, Saint-Petersburg, Russia.*

Sulfur K-edge X-ray absorption near edge structure (XANES) spectra have been recorded of aqueous sodium sulfite solutions at different pH values and of sulfur dioxide solutions. The XANES spectra are significantly different for the various species in the environmentally important sulfite(IV) system. Evaluation of the sulfur 1s electron excitations by means of Density Functional Theory – Transition Potential (DFT – TP) calculations provided insight into the coordination, bonding and electronic structure. At intermediate pH (~4) the two coordination isomers, the sulfonate (HSO_3^-) and hydrogen sulfite (SO_3H^-) ions with the hydrogen atom coordinated to sulfur and oxygen, respectively, could be distinguished with the ratio HSO_3^- : SO_3H^- about 0.28 : 0.72 at 298 K. The relative amount of HSO_3^- increased when increasing the temperature from 275 K to 343 K. For the sulfur dioxide molecule, $SO_2(aq)$, which dominates in strongly acidic ($pH < -1$) aqueous sulfite solution, the effect of hydration on the XANES spectra has been studied, as also for the sulfite ion, SO_3^{2-}. XANES spectra of sulfonate, methane-, trichloromethane- and trifluoromethanesulfonate compounds, all with closely similar S–O bond distances in tetrahedral coordination, were interpreted by DFT–TP computations. The energy of their first main electronic transition from the sulfur K-shell is about 2478 eV. The additional absorption features are similar when a hydrogen atom or an electron donating methyl group is bonded to sulfur. Significant changes occur for the electronegative trichloromethyl ($-CCl_3$) and trifluoromethyl ($-CF_3$) groups, which strongly affect the distribution of □ electrons around the sulfur atom. Raman and infrared absorption spectra of the $CsHSO_3$, $CsDSO_3$, CH_3SO_3Na and $CCl_3SO_3Na\cdot H_2O$ compounds, and Raman spectra of the sulfite solutions, have been interpreted by normal coordinate calculations. The C–S stretching force constant for the $Cl_3C-SO_3^-$ ion obtains an anomalously low value due to steric repulsion between the CCl_3 and SO_3 groups.

TK1

Application of the Specific Ion Interaction Theory (SIT) for the Ionic Products of Highly Concentrated Aqueous Electrolyte Solutions

Pál Sipos* and Tamás Gajda

University of Szeged, Department of Inorganic and Analytical Chemistry, H–6701, Szeged, Hungary PO Box 440.

When the Brönsted-Guggenheim-Scatchard Specific Ion Interaction Theory (SIT) is applied for the ionic product of water, pK_w, one obtains the equation

$$pK_w(m) + \frac{2A\sqrt{I(m)}}{1+B_{aj}\sqrt{I(m)}} + \log a_w = pK_w^0 + \Delta\varepsilon \cdot I(m)$$

where $pK_w(m)$ and pK_w^0 are molal ionic products at $I(m)$ and $I(m) \to 0$ molal ionic strengths, respectively, $A = 0{,}509$ and $B_{aj} = 1.5$, a_w is the actual water activity and $\Delta\varepsilon$ is the sum of the specific ion interaction coefficients, and is characteristic to the ions present in the system.[1]

If the left hand side of the equation is plotted against $I(m)$, the SIT predicts linear behavior, i.e., constant $\Delta\varepsilon$. It is however, generally thought[1], that such linearity can be expected only for solutions of $I(m) \leq 3.5$ mol kg^{-1}. Good quality equilibrium constants at $I(m) > 3.5$ mol kg^{-1} are scarce, this is the most likely reason, why the predictive power of SIT for solutions with background electrolyte concentrations of >3.5 mol kg^{-1} has not yet been investigated.

To explore the behavior of the SIT approach at high ionic strength, the model has been employed for the pK_w values determined in highly concentrated aqueous solutions of NaCl ($I(m) \leq 5.61$ mol kg^{-1}), KCl ($I(m) \leq 4.57$ mol kg^{-1}), CsCl ($I(m) \leq 10.02$ mol kg^{-1}), KBr ($I(m) \leq 4.71$ mol kg^{-1}), KI ($I(m) \leq 6.96$ mol kg^{-1}), $NaClO_4$ ($I(m) \leq 13.66$ mol kg^{-1}), and $(CH_3)_4NCl$ ($I(m) \leq 12.82$ mol kg^{-1}) at 25 °C. The pK_w values were selected from accurate literature data (see. refs. 2 – 4 and the references cited therein). From the plots thus obtained we concluded, that (i) no systematic deviation from linearity is observed up to $I(m) \leq 7$ mol kg^{-1}; (ii) the intercept of the plots, pK_w^0 (even with the inclusion of data points at the highest ionic strength) is 14.00 ± 0.02 (excluding the 13.93 value obtained for $(CH_3)_4NCl$ containing solutions); (iii) systematic deviation from linearity can only be clearly identified in the $I(m) >$ 8 mol kg^{-1} range (*i.e.*, for CsCl, $NaClO_4$ and $(CH_3)_4NCl$); (iv) this deviation is present as a downward curvature on the SIT plots; (v) $\Delta\varepsilon$ values obtained as the sum of $\varepsilon(OH^-,M^+)$ and $\varepsilon(H^+,A^-)$ calculated from the osmotic coefficient data of HA and MOH solutions are always somewhat larger than those determined from the linear sections of our SIT plots for the given MA salt; (vi) the lower limit of the specific ion interaction coefficient $\varepsilon(OH^-,(CH_3)_4N^+)$ have been calculated and, as expected for a non-complexing cation, it was found to be significantly higher, than those obtained for the other alkaline metal ions studied. On the basis of the results presented here, linear SIT behaviour could be expected for equilibria other than the autoprotolysis of water, up to ionic strengths significantly higher than 3.5 mol kg^{-1}.

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OS

Structure Refinement Methods Applied to Neutron and X-ray Diffraction Data on Water and Aqueous Solutions

A.K. Soper

ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, UK.

The past few years have witnessed a major revolution in the way diffraction data from water and solutions are interpreted. In the past a typical diffraction experiment would consist of one or more measurements on a particular system at a specified concentration in which the isotope neutron contrast was different for each sample. These data were then analyzed by a process of adding and subtracting datasets to extract a set of so-called composite partial structure factors (CPSF), which would in principle give more specific information about correlations associated with specific atomic sites than was obtainable with a single diffraction measurement on its own. These CPSFs would in turn, by a rather laborious trial and error process, be Fourier inverted to yield the corresponding weighted sum of individual site-site radial distribution functions (SSRDF).[1] While this process often gave useful results it lacked one important feature: there was no easy way of checking the reliability of estimated structure in a situation where the number of available diffraction contrasts was usually markedly smaller than the number of individual SSRDFs needed to define the structure of the system. Recently this approach has been superseded by a method based on computer simulation.[2] In the newer method, the amount of pre-massaging that is done to the data prior to structure refinement is kept to an absolute minimum. Instead the corrected diffraction total differential cross sections are used as the basic inputs to the structure refinement process, with the relationship to individual SSRDFs being defined by a matrix inversion of the scattering weights. The advantage of this scheme is that the relative emphasis of the data in the structure refinement can be varied, as can the underlying reference potential that seeds the simulation. This means a range of structures, all of which should be consistent with the diffraction data, are in principle accessible. This allows us to establish which estimated structures in the solution derived from the data are reliable and which are not reliable. Most recently the technique has been modified to allow both X-ray and neutron diffraction data to be refined simultaneously alongside each other, which results in a substantial improvement in the reliability of the structure reconstruction.[3] The talk will be illustrated with a selection of examples from structure refinements in pure water, non-ionic solutions such as alcohols, acetone, DMSO and urea, and monovalent ionic solutions.

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CS2

Experimental Study of Nd, Eu and Ho Hydrolysis at Elevated Temperatures by Spectrophotometric Method

S.A. Stepanchikova* and R.P. Biteikina

Institute of Geology and Mineralogy, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090, Russia.

Published data on the hydrolytic properties of lanthanoides are not numerous and when obtained in various experimental conditions are often noncomparable with each other. For example, according toWood[1], log of monohydroxocomplexes La, Eu, Gd and Yb stability constants measured by various techniques at 25 °C and ionic strength from 0.1 to 3.0 differed in interval from 4 to 8. So there is not of correlation with ionic strength and presence of higher order hydroxo complexes. This is a reason for the wide dispersion of experimental stability constants, which is observed even for a single element at the same ionic strength at elevated temperatures[2]. The study of the hydrolytic equilibria in Nd, Eu and Ho^{3+} solutions at 25 °C as well a temperature influence on their speciation has been carried out and is presented now. The special spectrophotometric method with a 2-naphtol as pH- indicator at temperatures up to 150 °C and ionic strength no more then 0.004 was used for. A complexation comparative analysis of Nd, Eu and Ho as representatives of lanthanoids separate groups is discussed in terms of their basicity.

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TK3

Solvent Composition Effects on Relaxation of Bulk Water Molecules and on Water Molecule Exchange Reaction of Aquanickel(II) in Aqueous Mixed Solvents with 2-Propanol or 1-Propanol

Masaaki Tabata,* Masayuki Baba, Eisi Goto and Toshiyuki Takamuku

Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840–8502, Japan; fax: +(81)952–28–8560;tabatam@cc.saga-u.ac.jp

Relaxation rates of free water molecules and the substitution rate of bound water molecules to nickel(II) ion have been studied by the ^{17}O–NMR method in mixed solvents of water and 2-propanol or 1-propanol containing 1.0 mol dm^{-3} NaClO$_4$ at different mole fractions of 2-propanol and at 243~303 K.

To get information on the general physical properties of the mixed solvent, we measured their melting points by differential scanning calorimetry (DSC). Samples of the mixed solvents were cooled and heated at a rate of 4.0 K/min over 293 ~148 K. The melting points gradually decreased with the propanol content in water, but showed an inflection point at 0.2 mole fraction where structural change from water clusters to 2-propanol cluster occurs.

The ^{17}O spin-lattice relaxation rate R_1 (= $1/T_1$), is related to the rotational correlation time τ_{rot} via the following equation,

$$R_1 = \frac{1}{T_1} = 3\left[\frac{2I+3}{40I^2(2I-1)}\right]\left[\frac{e^2qQ}{\hbar}\right]^2\left[1+\frac{\eta^2}{3}\right]\tau_{\mathrm{rot}}.$$

The R_1 values were determined at different mole fractions of 2-rpopanol and at a temperature range from 303.15 to 258.15 K. The plot of ln τ_{rot} vs. $T^{-1}/10^3$ K^{-1} gave a straight line. The activation energy (E_a/kJ mol^{-1}) was determined from the Arrhenius equation. The values are shown in Figure 1 as a function of mole fraction of 2-propanol. The activation energy reaches a maximum by 0.1 mole fraction of 2-propanol and decreases again, suggesting significantly strengthened hydrogen bonds of water molecules with increase in 2-propanol.

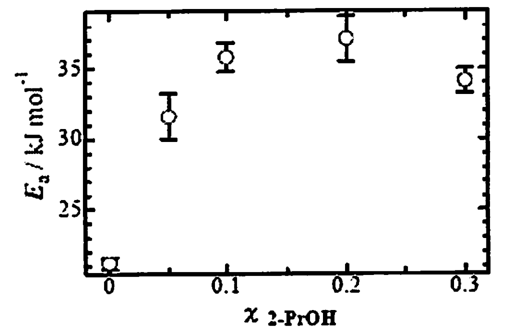

Figure 1: Activation energies at different mole fractions of 2-PrOH.

The water exchange rate of Ni(H$_2$^{17}O) was measured at the same mole fractions and temperatures. Activation free energy ($\Delta G^‡$) was independent of the mole fraction, but the values of $\Delta H^‡$ and $-T\Delta S^‡$ compensated each other and gave minimum and maximum at 0.1 mole fraction of 2-propanol.

Combining the results of three different methods, the effects of solvent composition on water exchange rate are discussed.

IL1

X-ray Diffraction Study on Structure of Imidazolium Ionic Liquids

Toshiyuki Takamuku,[a*] Kenta Fujii,[a] Ryo Kanzaki,[b] Yasuhiro Umebayashi,[b]
Shin-ichi Ishiguro [b] and Toshio Yamaguchi [c]

[a] *Department of Chemistry and Applied Chemistry, Faculty of Science and Technology, Saga University, Honjo-machi, Saga 840–8502, Japan;*
[b] *Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812–8581, Japan;*
[c] *Advanced Materials Institute and Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814–0180, Japan.*

Recently, room-temperature ionic liquids have attracted much attention since they can be use in various application fields, such as a lithium secondary battery, organic synthesis, and polymerization, as a novel solvent due to their unique properties, such as non-combustibility and non-volatility. However, the origin of such physicochemical properties is not well understood. The structure of ionic liquids is essential to understand their properties and chemical reactions in them. We have made X-ray diffraction experiments on two imidazolium ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMI^+BF_4^-$, m.p. = 16 °C) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($EMI^+Tf_2N^-$, m.p. = –15 °C) to clarify their liquid structure at the molecular level. Based on the results from the X-ray diffraction measurements together with those of ^1H, ^{13}C and ^{19}F NMR experiments, Raman scattering, density functional theory (DFT) calculation, and molecular dynamics (MD) simulation, the structure of ionic liquids was elucidated. EMI^+ is in equilibrium between planar and nonplanar conformations, where the ethyl group is positioned in the same plane of the imidazolium and stands up from the plane, respectively, in both ionic liquids.[1] In $EMI^+BF_4^-$, four BF_4^- interact with the imidazolium ring of EMI^+. In $EMI^+Tf_2N^-$, Tf_2N^- has two conformations of C_1 and C_2 forms, where two trifluoromethyl groups are set at cis and trans positions with respect to the S–N–S bond, respectively.[2] Several EMI^+ and Tf_2N^- interact with each other to form clusters in the liquid. On the basis of the structure of both ionic liquids, their unique properties will be discussed.

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CS1

Solvation Structure of Li^+ in Concentrated $LiPF_6$–Propylene Carbonate Solutions
– Time-of-Flight neutron diffraction and MD simulation –

Munetaka Takeuchi,[a,c*] Yasuo Kameda,[b] Yasuhiro Umebayashi,[c] Mohanmmad Abdul Wahab,[c] Shuhei Fukuda,[c] Shin-Ichi Ishiguro,[c] Motoya Sasaki,[b] Yuko Am, [b] Takeshi Usuki [b]

[a] Fujitsu Limited, Chiba 261–8588, Japan;
[b] Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Kojirakawa-machi 1–4–12, Yamagata 990–8560, Japan;
[c] Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, 812–8581, Japan.

In most of the lithium ion secondary batteries electrolyte are constituted of $LiPF_6$ as the solute and propylene carbonate (PC) as main solvent because the solution can practically perform the highest conductivity. In order to obtain structural information on the first solvation shell of Li^+, Time-of-Flight (TOF) neutron diffraction measurements[1] and Molecular Dynamics (MD) simulation[2] were carried out for $LiPF_6$ – PC solutions. TOF neutron diffractions were executed for $^6Li/^7Li$ isotopically substituted 10 mol% $LiPF_6$ – PC–d_6 solutions. In the results, structural parameters concerning the nearest neighbor $Li^+\cdots PC$ and $Li^+\cdots PF_6^-$ interactions were determined through the least squares fitting analysis of the observed difference function, $\Delta Li(Q)$. It has been revealed that the first solvation shell of Li^+ consists of 4.5(1) PC molecules with the intermolecular $Li^+\cdots O(PC)$ distance of 2.04(1) Å. The bond angle, $\angle Li^+\cdots O{=}C$, has been determined to be 138(2)°. $Li^+\cdots F(PF_6^-)$ distance, 2.98(1) Å, is much larger than the sum of ionic radius of Li^+ ion and van der Waals radius of F atom ($0.59 + 1.47 = 2.06$ Å). This suggests that the $Li^+\cdots PF_6^-$ contact ion pair is little formed in the present solution, though the formation of the $Li^+\cdots PF_6^-$ *ion pair* in PC was proposed from electrochemical measurements. It should be noted that there are 9 solvent PC molecules per one Li^+ ion and one PF_6^- ion in the concentrated 10 mol% $LiPF_6$ solution of PC. Therefore, most of the ions may exist as at least the *solvent shared* and *solvent separated* ion pairs in such a concentrated solution. The present MD simulation revealed that $LiPF_6$ solution has little $Li^+\cdots PF_6^-$ *ion pair* while $LiBF_4$ – PC solution has many *ion pairs.* Evidently, the present study revealed that the PF_6^- ion dominantly exists in the second or higher solvation sphere of the Li^+ ion.

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TK1

Chemical Species of Silica in Tokyo Bay: Change of Silica Species Based on the Solution Character

Miho Tanaka,[a]* Kazuya Takahashi,[b] Masao Nemoto [a] and Hideki Nagashima [a]

[a] *Tokyo Univ. of Marine Sci. and Tech 108–8477 Tokyo, Japan*
[b] *RIKEN, Saitama 351–0198, Japan*

The authors have studied the dissolution system of silica into solutions, *as they were*, using FAB–MS(fast atom-bombardment mass spectrometry)[1,2]. The results of speciation of silica in solution has been examined comparing with the data of ^{29}Si NMR, and characterized on the basis of the relative peak intensity of silica species observed by FAB–MS. In these studies, dimer($Si_2(OH)_5O_2^-$ m/z 173), linear tetramer ($Si_4(OH)_9O_4^-$ m/z 329) and cyclic tetramer($Si_4(OH)_7O_5^-$ m/z 311) have been regarded as main species in solution. In the case of sodium chloride (NaCl) solution, the complexes of those species with sodium ion are also contained The solubility of silica depends on the concentration of co-existing salts in many cases such as NaCl, while it is maximized at some concentration of co-existing salts, that is the salting-out effect. At this effect, not only the total concentration of silica but also the distribution of silica species in the solution changed. It is considered that the dissolved silica species are ruled by complex factors, such as the solubility of silicate complexes, the increase in the concentration of different kinds of soluble silicate complex induced by changes in the hydrophobicity and hydrophilicity of the solution, and the contribution of hydrolysis.[3]

In seawater, the concentration of silica is not so high that only the salting-out effect would rule the dissolution of silica and its behavior. It was expected to characterize the solution system from the delicate changes of silica species, because the silica concentration and the other physical data could not distinguish the character of seawater. Silica is one of the nutrients in seawater as well as nitrate and phosphate, while the role of silica is not elucidated for uptake by the diatom. The authors have examined the seawater in Tokyo Bay, based on the speciation by FAB–MS, to classify the silica species into the species feeding the diatom or not feeding. From seasonal change of silica species in Tokyo Bay, it has been found that the dimmer and linear tetramer is "main" food to the diatom resulted from the ratios of dimmer/cyclic tetramer and linear tetramer/cyclic tetramer. Those ratios also revealed that the dimmer and linear tetramer were lacked from April to October in the open sea, while in Tokyo Bay, they were lacked in July. And the seasonal changes of the distribution of silica species according to the depth have been shown as a typical distribution in annual changes.

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TK3

Time-Resolved Enthalpies, Heat Capacities and Translational Diffusion of Reaction Intermediates of Biological Proteins

Masahide Terazima

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Japan.

The thermodynamics and diffusion process have been playing very important roles to reveal the nature of molecules or the state of substances in solution. The thermodynamical properties; molecular volume, enthalpy, entropy, thermal expansion coefficient, and so on have been considered to be fundamental properties to describe the states. Because of the importance, a variety of techniques to measure these quantities 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 thermodynamical and diffusion properties are not easily accessible for transient species. Recently our group has been working on the time-resolved studies of thermodynamical as well as transport properties during a variety of photophysical and photochemical processes. The studies include ultrafast detection of temperature increase after the nonradiative transition, time-resolved detection of enthalpies and volume changes without any temperature or pressure variation. Here I will report the time-resolved thermodynamical and time-resolved diffusion measurements of some biological proteins performed in our group. We stress that measurement of volume or energy changes in the time domain opens up a new and interesting area for kinetic studies.

We used the pulsed laser induced transient grating and transient lens methods for quantitative measurements of the diffusion, partial molar volume change, and the enthalpy change during a photochemical reaction in time domain without any assumption for the first time. We applied this technique to the photochemical reactions of various proteins. Here we will show studies on conformational change of photoactive yellow protein (PYP).

PYP is a relatively small (14 kDa) water soluble protein, which has a function of a blue light photoreceptor for a negative phototactic response. Upon flash excitation of PYP, the ground state (pG) is converted into red-shifted intermediate pR in less than 2 ns. Subsequently, pR decays on the sub-millisecond time scale into blue shifted intermediate pB. This pB returns to pG in seconds time scale. We found that the heat capacity of the short lived intermediate pR is the same as that of the ground state species within our experimental accuracy, whereas that of the long lived intermediate pB is much larger than that of pG. The larger heat capacity is interpreted in terms of the conformational change of the pB species such as melted conformation and/or exposure of the non-polar residues to the aqueous phase. Furthermore, it was found that the diffusion coefficient of pB is much smaller than that of pG. The reduction of the diffusion coefficient was attributed to the enhanced intermolecular interaction with water on pB. This technique can be used for photochemical reaction in general to investigate the conformational change and the hydrophobic interaction in time domain.

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NS1

Ternary Diffusion Coefficients for Zwitterionic Surfactant–Ionic Surfactant–Water Systems

Toshihiro Tominaga,* Hiroshi Iwata and Yuya Kato

Department of Applied Chemistry, Okayama University of Science, 1–1 Ridai-cho, Okayama 700–0005, Japan.

Mutual diffusion coefficients for binary systems of ionic surfactants and water are larger than those of non-ionic or zwitterionic surfactants and water at surfactant concentrations above critical micelle concentrations (CMCs). We have studied how mutual diffusion coefficients increase when a long-chain ionic surfactant is added to micellar solutions of a zwitterionic[1] or non-ionic[2] surfactant. In the case of three component systems containing two solutes (components 1 and 2) and solvent (component 0), fluxes of components 1 and 2, J_1 and J_2, respectively, are written as

$$J_1 = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \tag{1}$$

$$J_2 = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \tag{2}$$

In this study, we used a zwitterionic surfactant, N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (C_{14}DAPS) as component 1, an ionic surfactant, alkyltrimethylammonium halide (C_nTAX) as component 2, and water as component 0. Diffusion coefficients were measured by the Taylor dispersion method. Into solution A that contains C_1 and C_2 of components 1 and 2 and is flowing through a capillary tube under a laminar flow condition, a small amount of solution B that contains $C_1 + \Delta C_1$ and $C_2 + \Delta C_2$ of components 1 and 2 was injected. Solutes were dispersed along the tube as a result of diffusion and convection, and the solute distribution was detected at the end of the tube by a differential refractometer. At various combinations of initial ΔC_1 and ΔC_2, solute distributions at the end of the tube were analyzed, and D_{ij} values were obtained.

For C_nTAX having dodecyl, tetradecyl, hexadecyl, and octadecyl chains, the D_{12} values are much larger than D_{11} values. This is interpreted as due to the fact that the solubilization of C_nTAX (n = 12, 14, 16, and 18) into the C_{14}DAPS micelles increases the diffusion of the latter because of the electrostatic attraction of counter ions (Br^- or Cl^-) whose diffusivities are much higher. Other D_{ij} values can be interpreted in terms of the degree of solubilization of C_nTAX into the C_{14}DAPS micelles.

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OS

Low-frequency Depolarized Raman Scattering of Supercritical Water

Yasunori Tominaga,[a*] Mika Murai [a] and Yuko Amo [b]

[a] *Depart. of Physics and Chemistry, Ochanomizu University, Tokyo 112–8610, Japan;*
[b] *Department of Materials and Biological Chemistry, Yamagata University., Yamagata 990–8560, Japan.*

Low-frequency depolarized Raman scattering spectra of liquid water from –250 $\mathrm{cm^{-1}}$ (–7.5 THz) to 250 $\mathrm{cm^{-1}}$ (7.5 THz) including supercritical region have been obtained and analyzed by using the MRT(Multiple Random Telegraph model) relaxation function which takes into account the inertia and memory effects on fluctuation. The critical point of water is $T_c = 374$ °C (647 K) and $P_c = 22.1$ MPa, and the critical density is $\rho = 0.322$ $\mathrm{g/cm^3}$. It is very important to investigate the characteristics of hydrogen-bond of supercritical water in order to reveal the anomalous nature of liquid water.

Low-frequency Raman scattering is an effective method to study molecular dynamics in liquids. Particularly depolarized low-frequency Raman spectra give the Fourier transform of the time correlation of fluctuating polarizability produced by inter-molecular collective motions and/or relaxational motions. In the previous paper we have reported the first observation of the low-frequency Raman spectra towards to and above the supercritical point with constant pressure at 25 MPa.[1] In the present paper we have carried out the low-frequency Raman scattering experiments along the vapor pressure curve toward to the supercritical region.

Raman scattering spectra were obtained by a double grating monochromator (Jobin–Yvon U–1000). The volume of sample water in a pressure cell is about 1.5 $\mathrm{cm^3}$. The 3 sapphire windows of 30 mm ϕ are used together with quartz backup windows for a pressure cell. The effective radius of the windows is about 15 mm ϕ.

The Raman spectral intensity $I(\nu)$ is reduced to the imaginary part of dynamical susceptibility (reduced Raman spectra) $\chi''(\nu)$ ($\propto \varepsilon''(\nu)$) through dividing by the Bose-Einstein factor. The spectral fittings have carried out by a superposition of the MRT relaxation function and damped harmonic oscillators.

The 180 $\mathrm{cm^{-1}}$ (5.4 THz) band as well as 50 $\mathrm{cm^{-1}}$ (1.5 THz) band have vanished with decreasing density. Below about $\rho \fallingdotseq 0.6$ $\mathrm{g/cm^3}$ the low-frequency Raman spectra are well fitted by only one MRT relaxation function with the background of broad libration modes around 800 $\mathrm{cm^{-1}}$ (24 THz). This vanishing of inter-molecular vibration modes are due to the destruction of hydrogen-bonds. The obtained relaxation time first decreases and then increases from about $\rho \fallingdotseq 0.8$ $\mathrm{g/cm^3}$ with decreasing density and in the supercritical region the increase of the relaxation time is almost linearly. This behavior is consistent with that of the dielectric relaxation time.[2] In the supercritical region the relaxation time obtained from Raman spectra gradually tends to that of dielectric relaxation time in ref.2. This must reflect the characteristics of hydrogen-bonds of water in the supercritical region.

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SS1

Structure Determination of Hydrated, Hydrolyzed and Solvated Thorium(IV) Ions in Solution and Solid State

Natallia Torapava* and Ingmar Persson

Department of Chemistry, Swedish University of Agricultural Sciences, Uppsala, Sweden.

The chemical properties of metal ions in solution are reflected in the structure of the hydrated and solvated ions. Structural information is therefore important to understand and assess peculiarities e.g. how the properties of the actinoid(III) and (IV) ions change within the series, and how these affect different natural and technological processes taking place in aqueous solution. In this work EXAFS (extended X-ray absorption fine structure) spectroscopy and crystallography were used to get information about the structures of hydrated, hydrolyzed and solvated thorium(IV) in solid state and solution. EXAFS gives information about the distances to thorium, the bond distance distribution, and an estimation of the coordination number.

The crystal structure of $[Th(H_2O)6(\mu_3\text{–}ClO_4)](ClO_4)_3\cdot H_2O$ shows that thorium(IV) is nine-coordinated, and that thorium binds six water molecules and three oxygens from one perchlorate anion. The same coordination number is found in the complexes of the salt precipitating out from an acidic aqueous solution of thorium(IV) trifluoromethanesulfonate, $[Th(OSO_2CF_3)_3(H_2O)_6]_2[Th(OSO_2CF_3)_6(H_2O)_3]$. The hydrated thorium(IV) ion in aqueous solution have the same configuration (nine-coordination) as in the solids but no counter ions are bound to the thorium(IV) ion in aqueous solution. The structure of hydrolyzed thorium(IV) ion at pH 1.96 (the pH where precipitation of ThO_2 starts) is a binuclear thorium(IV) complex with double hydroxo bridges. The Th – O bond distance is ca. 0.10 Å shorter to the bridging hydroxo groups than to the approximately seven terminal water molecules, 2.35 and 2.45 Å, respectively. The structures of the dimethylsulfoxide (dmso) and *N,N'*-dimethylpropyleneurea (dmpu) solvated thorium(IV) ions have been studied in solution showing coordination numbers of eight and seven with Th–O bond distances of 2.42 and 2.38 Å, respectively. A short overview of the structures of the hydrated actinoid(IV) ions in aqueous solution will be given.

CS2

Solution Chemistry of Polynuclear Complexes Containing $[M_3Ln_2(L)_6]$ Units (M: 3d Transition Metal Ions, Ln: Lanthanide Ions, L: Oxydiacetate or Iminodiacetate)

Julia Torres,[a]* Florencia Peluffo,[a] Paula Morales,[a] Sixto Domínguez [b] and Carlos Kremer [a]

[a] *Cátedra de Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, CC 1157, Montevideo, Uruguay.*
[b] *Departamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Canary Islands, Spain.*

Polynuclear complexes are widely regarded as potential materials in separation, catalysis, gas storage and molecular recognition. The inclusion of lanthanides in the heterometallic complexes offers structural flexibility, and increases the thermodynamic stability. Up to now, the studies on these heteropolynuclear complexes have been mostly focused on lanthanide copper compounds at solid state. We have expanded this knowledge to the solution chemistry, in particular to investigate if such polynuclear species can also exist in aqueous solution. If so, the complexes would be potential homogeneous catalysts for many processes. Besides, we have studied the effect that a change in the 3d metal ion, the lanthanide ion or even the ligand (changing the coordinating ether site by amino) causes to these structures. In this work, potentiometric titrations performed at 25.0 °C, and $I = 0.5$ M Me_4NCl were carried out. We found that polynuclear units can be formed with M(II) (Cu, Mn, Ni, Fe, Co, Zn, Pb, Cd, Be) and M(III) (Fe, Al) ions, with various lanthanides (La, Ce, Sm), and that they can be predominant in aqueous solution. With a few exceptions, the studied cations can exist in solution as $[Ln_2M_3(L)_6]$ or $[Ln_2M_3(L)_6(OH)_n]^{n-}$ (n = 3, 6), representing the same 2:3:6 stoichiometry generally found at solid state. Trivalent cations, Fe(III) and Al(III), like most +2 cations, also predominate as a 2:3:6 species, but in this case with a higher degree of deprotonation. The presence of an amino group in the ida ligand makes formed complexes with 3d metal ions more stable, preventing in some extent the formation of polynuclear complexes.

TK3

Naked Tl-Pt Bonded Cyano Complexes: New Results

Imre Tóth,[a*] Mihály Purgel,[a] Mikhail Maliarik [b] and Julius Glaser [c]

[a] *Department of Inorganic and Analytical Chemistry, University of Debrecen, H–4010 Debrecen, Hungary;*
[b] *IFM–Department of Chemistry, Linköping University, SE–581 83 Linköping, Sweden;*
[c] *Department of Chemistry, Inorganic Chemistry, Royal Institute of Technology (KTH), SE–100 44 Stockholm, Sweden.*

Recently, we have reported studies on the formation, structure and equilibrium of a new family of oligometallic platinum-thallium cyano compounds containing a direct metal-metal bond.[1,2] The complexes are synthesized according to the reaction:

$$m\mathrm{Pt(CN)_4}^{2-} + \mathrm{Tl}^{3+} + n\mathrm{CN}^- \rightleftharpoons [\mathrm{Pt}_m\mathrm{Tl(CN)}_{4+n}]^{(n-1)-}$$

Four binuclear species represented by a general formula $[(NC)_5Pt–Tl(CN)_{n-1}]^{(n-1)-}$ ($n = 1 – 4$) and a trinuclear complex $[(NC)_5Pt–Tl–Pt(CN)_5]^{3-}$ are formed in aqueous solution.

The complexes exist in an equilibrium, which also includes the parent complexes $Pt(CN)_4^{2-}$ and $Tl(CN)_n^{3-n}$ ($n = 0 – 4$), and can be controlled by varying the cyanide concentration and/or pH of the solution.

Multinuclear NMR- (^{13}C, ^{195}Pt, ^{205}Tl), IR-, Raman-, ESCA-spectroscopy, X-ray and EXAFS studies confirm direct, sort (2.60 – 2.64 Å) Pt–Tl bonds, formed as a four electron three center bond. Formation kinetics of the complexes involve at least two steps: (i) Pt–Tl bond formation by an one electron transfer reaction and (ii) formation of the $-Pt(CN)_5$ unit by entering a cyanide ligand. Detailed mechanism of the reactions is suggested.[3]

The compounds are usually inert towards redox decomposition and can be kept in solution for years in the dark at room temperature. Under certain conditions a two-electron transfer reaction between the bound platinum and thallium atoms takes place. The only product of thallium reduction is Tl(I), while oxidation of platinum leads to different complexes of either Pt(IV) or Pt(III), including two new compounds:[4] $(CN)_5Pt^{IV}(H_2O)^-$ and $(CN)_5Pt^{III}Pt^{III}(CN)_5^{4-}$.

Experiments to prepare analogs with Pd(II), Ni(II) instead of Pt(II) or Hg(II) to substitute Tl(III) resulted in different type of compounds.[5]

The work was supported by the OTKA K63388 research grant.

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TS2

Multiscale Description of Charged Liquids and Confined Media

Pierre Turq,* Vincent Dahirel, Benjamin Rotenberg, Jean François Dufrêche and Marie Jardat

Université Pierre et Marie Curie, Paris, France.

Complex ionic or colloidal solutions and confined-charge media are unsuitable for simple solvent-averaged descriptions such as the Debye-Hückel/Poisson-Boltzmann approximations. It is necessary to take into account specific features such as those coming from the geometric exclusion boundary conditions and the far from infinite dilution situation. For colloidal solutions, counterion averaging of Brownian dynamics (BD) can provide efficient alternatives to classical DLVO theories, by a suitable coarse graining procedure. For charged confined media, molecular dynamics simulation results can be reproduced with a Fokker-Planck equation, which can be solved by a lattice model. In both cases, a bridge can be constructed, which links the dilute solution region and continuous solvent models and the concentrated solutions discrete solvent descriptions.

1) Colloidal solutions. A multiscale strategy based on the BD simulation method is presented. It leads to an approximate but realistic reproduction of the dynamics of charged nanoparticles in suspension. This method is particularly suited to systems containing highly dissymmetric electrolytes with added salts, like micellar suspensions or protein solutions. 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 rigorously averaged out. Our contribution aims at quantitatively evaluating the influence of the eliminated forces on the nanoparticle dynamics. For this purpose, an effective diffusion coefficient has to be calculated. In practice, this effective diffusion coefficient is taken as an input of a coarse-grained simulation that uses the potential of mean force between nanoparticles. Our procedure has been validated by the quantitative comparison between coarse-grained calculations and BD simulations at the "microscopic" level (which explicitly includes microions). For a model of aqueous solutions of 10–1 electrolyte with a 1–1 added salt, the agreement is excellent. This method allows us to compute diffusion coefficients of nanoparticles one order of magnitude faster than with explicit BD.

2) Charged porous media. Particle mobility is generally lowered by a confining medium because of geometrical effects and interactions with the confining surfaces (especially if charged). The water/mineral interface plays a central role in ion dynamics: ionic mobility in clays is often understood as an interplay between the diffusion of mobile ions and their possible trapping at the mineral surfaces. We describe how to build a two-state diffusion-reaction scheme from the microscopic dynamics of ions, controlled by their interaction with mineral surfaces. The starting point is an atomic description of the clay interlayer using molecular simulations. These provide a complete description of the ionic dynamics on short time and length scales. Using these simulation results, we build a robust mesoscopic (Fokker-Planck) description, which is used to determine the mobility of the ions in the interlayer. These results can then be cast into a diffusion-reaction scheme, introducing in particular the fraction of mobile ions, or equivalently the distribution coefficient K_d. This coefficient is of great importance in characterizing electrokinetic phenomena in porous materials.

IL2

Lithium Ion Solvation in Bis-(trifluoromethanesulfonyl) Imide type Room Temperature Ionic Liquids: DFT Calculations and Raman Spectroscopic Study

Yasuhiro Umebayashi,[a]* Takushi Mitsugi,[a] Takao Fujimori,[a] Shuhei Fukuda,[a] Kenta Fujii,[b]
Ryo Kanzaki,[a] Munetaka Takeuchi [a,c] and Shin-Ichi Ishiguro [a]

[a] *Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, 812–8581, Japan;*
[b] *Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga 840–8502, Japan;*
[c] *Fujitsu Limited, Chiba 261–8588, Japan.*

Lithium ion solvation structure in bis-(trifluoromethanesulfonyl) imide (Tf_2N^-)type Room Temperature Ionic Liquids consisting of imidazolium and pyrrolidium cations was studied by Raman spectroscopy and DFT calculations. Raman spectra of Tf_2N^- ionic liquid, 1-ethyl-3-methylimidazolium (EMI^+), containing 0.144 – 0.589 mol dm^{-3} $Li^+Tf_2N^-$ salt were measured at 298 K over the wide frequency range. The intense 744 cm^{-1} Raman band ascribable to free Tf_2N^- ion shifted to higher frequency at 750 cm^{-1}, whose intensity increased with increasing lithium ion concentration. The band intensities were analyzed to evaluate the solvation number of lithium ion. Thus evaluated solvation number was 1.88(1), which indicates the lithium ion shows tetrahedral solvation structure coordinated by two Tf_2N^- ions with bi-dentate manner. On the other hand, the 279, 297, 396 and 406 cm^{-1} Raman bands ascribable to the C_2 isomer of Tf_2N^- anion decreased, while 288, 315, 328, 343 and 353 cm^{-1} bands of the C_1 conformer increased. Moreover, the decrease of the 396 cm^{-1} band was more rapidly than that of 406 cm^{-1} one and a new Raman band appeared at around 420 cm^{-1}. These indicate that the C_1 conformer with larger dipole moment is more stabilized in the first solvation sphere around the lithium ion. The DFT calculations of the $[Li(C_1{-}Tf_2N^-)_2]^+$, $[Li(C_1{-}Tf_2N^-)(C_2{-}Tf_2N^-)]^+$ and $[Li(C_2{-}Tf_2N^-)_2]^+$ were carried out and the optimized geometries with no imaginary frequencies were successfully obtained. The SCF energy differences, □E_{SCF}, at the optimized geometries from $[Li(C_2{-}Tf_2N^-)_2]^+$ to $[Li(C_1{-}Tf_2N^-)(C_2{-}Tf_2N^-)]^+$ and $[Li(C_1{-}Tf_2N^-)_2]^+$ were 0.0 and 1.0 kJ mol^{-1}, respectively, which supports the experimental evidences.

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TK1

Characterization of Aluminum Species in Aqueous Solution by ESI–MS

Tatsuya Urabe,[a]* Miho Tanaka [a] and Takahisa Tsugoshi [b]

[a] *Tokyo Univ. of Marine Sci. and Tech., Tokyo, 108–8477 Japan;*
[b] *AIST, Tsukuba, Ibaraki 305–8563 Japan.*

The speciation of aluminum (Al) has been required. For example, Al is the third abundant element in the earth crust and coagulated with other elements at the estuary. Aluminum that is escaped from the deposition is poured into the sea and scavenged as interacting with other compounds. Therefore, Al is related to the global circulation in natural water. The elucidation of the Al dynamics in natural water requires not only the estimation of the total concentration, but also the determination of the chemical forms of Al species. We have carried out the Al speciation with electrospray ionization mass spectrometry (ESI–MS) to identify Al species in aqueous solution.[1] ESI–MS has high sensitivity for the detection of Al species and requires only a short analysis time compared with ^{27}Al–NMR. In addition, the molecular formula of Al species is directory identified on the basis of *m/z* and ESI–MS can provide the new information for Al speciation in solution chemistry. In this study, several Al species were characterized with ESI–MS and the results were compared with those from other methods or the knowledge of chemistry. And the applicability of ESI–MS for the speciation of Al was discussed.

First, the interaction between Al ion and water molecule (i.e. hydrolysis of Al) was studied with ESI–MS. And characteristic Al species were identified at each pH value. In the low pH region, various Al species from monomer as a major species to pentamer were identified with ESI–MS, whereas other methods, such as ^{27}Al–NMR or potentiometric technique, could detect monomer and dimer only. This indicates that the hydrolysis of Al may not be so simple. In neutral pH region, characteristic Al species containing thirteen Al atoms (Al_{13}) was observed. Over the pH range, the distribution diagrams of Al species were very similar to those from ^{27}Al–NMR.[2] This strongly suggests that no critical chemical modification occurred in the gas phase and results from ESI–MS preserved the original chemical state in solution. When anions, such as sulphate ions forming stable complex with Al ions, coexisted in Al solutions, the hydrolysis of Al was not promoted and Al_{13} was not formed in the neutral pH region. That is, the speciation of Al is sensitive to coexisting compounds. Generally, chemical composition in natural water is very complicated and the formation of Al complexes with each coexisting ligand in natural water should be examined. Aluminum-ligand complex (such as $Al–SO_4$, Al–F complex) will be also examined and the applicability of ESI–MS as a new tool of Al speciation will be presented.

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TK2

Kinetics of G-Quadruplex Folding and Unfolding

Iztok Prislan, Jurij Lah and Gorazd Vesnaver*

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia.

Telomeres, the end of chromosomes, contain guanine-rich DNA sequences. Telomeric DNA preserves chromosome ends from damage and recombination. Although most telomeric DNA is double-stranded, the extreme 3′ end of the telomere consists of single stranded G-rich DNA over-hangs which under appropriate conditions of high Na^+ or K^+ ionic strength can form tetrameric structures. These structures, G-quadruplexes, adopt a variety of folds, dependent in part on whether they are intra- or inter-molecular. All quadruplexes contain the basic repeating motif, the G-quartet, which comprises four guanine bases held in plane by Hoogsteen hydrogen bonding.[1] To determine the molecularity of such quadruplexes together with the ΔG^0, ΔH^0 and ΔS^0 of their formation, a combination of several experimental methods has to be used.

NMR studies have shown that in aqueous solutions the d(G4T4G3) and d(G4T4G4) molecules in the presence of some cations form structures that exhibit properties characteristic of bimolecular quadruplexes.[2,3] In an attempt to investigate the conformational behavior of d(G4T4G3) and d(G4T4G4) structures formed in the presence of Na^+ and K^+ ions and to determine the thermodynamics of their formation we have employed a combination of spectroscopic (UV, CD) and calorimetric (DSC) techniques. Our results show that unfolding and folding of the two bimolecular quadruplexes involve several kinetic steps and thus cannot be described by simple equilibrium two-state thermodynamics. Consequently, we propose a mechanism for the observed temperature induced formation and dissociation of both quadruplexes and discuss it in terms of the corresponding activation energies.

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CS1

Thermodynamic Properties of $CaSO_4$ Dissolved in Concentrated Aqueous Electrolyte Solutions

W. Voigt* and G. Wollmann

Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, 09596 Freiberg, Germany. Wolfgang.Voigt@chemie.tu-freiberg.de

Dissolved $CaSO_4$ plays an important role in natural, geo-technical and industrial processes. Aspects are scale formation or membrane destruction in reverse osmosis or filter processes due to crystallization of gypsum and other. For solutions containing some seawater components as for instance NaCl detailed thermodynamic models were established to describe the solubility of $CaSO_4$ phases in dependence on electrolyte concentration, temperature and pressure[1–3]. The solubility of slightly soluble salts as gypsum or anhydrite represents an important source for thermodynamic activity data. However, there is no common understanding of its variation with concentration in terms of ionic interactions and ion hydration in the different type of electrolyte media. In the contribution all available solubility data of $CaSO_4$ phases in aqueous electrolyte solutions are analyzed to derive the mean activity coefficient $\gamma_\pm(CaSO_4)$. New data in the systems $CaSO_4$–MSO_4–H_2O (M = Mg, Mn, Co, Ni, Cu, Zn) are presented and included in the systematic analysis. Since the MSO_4 components do not form double salts with $CaSO_4$, activity coefficients $\gamma_\pm(CaSO_4)$ can be calculated straight forward in these systems until very high ionic strengths. Published association constants MSO_4[4] are not suited as a guidance to explain the individual variation of $\gamma_\pm(CaSO_4)$ in the solutions of different electrolytes.

The effect of ion pair formation[4] is discussed within the frame-work of solution models (specific ion interactions, Pitzer equations) and lattice model approaches for molten salts. On the one hand there are several models applicable to fit the data with equal success. On the other hand, for the development of predictive models the variation of parameters from system to system has to be correlated with more primary structural and energetic data from solid state structures and quantum chemistry.

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NS2

How Co-Ions Influence the Stability of Ionic Microemulsions

Wolfgang Wachter* and Richard Buchner

Institut für Physikalische und Theoretische Chemie der Universität Regensburg, 93040 Regensburg, Germany.

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

The influence of co-ions on the ternary system didodecyldimethylammonium bromide (DDAB) / water (W) / *n*-dodecane (D) is a typical example for this: At room temperature, a homogeneous L_2-microemulsion is formed over wide areas of the DDAB/W/D phase diagram, the surfactant cations being located almost entirely in the W/D-interface. However, adding bromide salts (XBr) to this system beyond a threshold concentration induces the shrinking of the stability region of the microemulsion to a tiny island, that remains constant against further electrolyte addition. The reason for this phenomenon is completely obscure, especially since the threshold concentration only amounts to 1 % of the total ion concentration. As the bromide concentration in the solution remains virtually constant at such a tiny electrolyte addition, it is obviously due to a cationic effect. The explanation proposed by Ninham et al.[1] assumes a highly cooperative effect, where the water molecules bound in the interface and their interactions with the co-ions play a decisive role. Elucidating this phenomenon would certainly mean a major step towards an understanding of the co-ion influence on the stability of ionic microemulsions and of polyelectrolyte solutions in general.

Thanks to its sensitivity to collective modes of hydrogen bond systems and the reorientation of transient dipolar aggregates dielectric relaxation spectroscopy (DRS) sheds some light on the dynamics of cooperative processes and on the structural consequences arising from that. This method appears to be particularly suitable for the investigation of the phenomenon described above, as it already revealed some characteristic relaxation processes caused by hydrate water molecules surrounding hydrophobic ions and micelles of various surfactants. Micelle-specific relaxation processes should also be detected.

This contribution presents a DRS study comparing the influence of the co-ions lithium, sodium, caesium and tetramethyl ammonium on the relaxation behaviour of DDAB/W/D microemulsions. Starting from an analysis of the effects of different univalent co-ions on DDAB/W/D the structure and dynamics of this ionic microemulsion system depending on its composition will be investigated.

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NS1

To Dissolve or Not To Dissolve: Sticking Coefficients of Organic Solutes at the Water Surface

W. Earle Waghorne,* Christina O'Farrell and Sedigh Noban

School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.

A gas phase molecule striking a liquid surface must either bounce off of the surface, remaining in the gas phase, or adsorb onto the surface, making dissolution possible. The sticking coefficient of a molecule is the probability that a collision will result in adsorption.

The collision between the gas phase and surface molecules takes place in around 10^{-11} seconds. This is relatively long, compared to vibrational frequencies (10^{-12} to 10^{-14} s^{-1}) but is short compared to the rotational frequencies (10^{-11} to 10^{-9} s^{-1}). Thus, there is time for interactions to form between surface and substrate molecules but not for reorientation of surface molecules to optimize these interactions and the sticking coefficients will be determined by the interactions that are formed with the surface molecules in their equilibrium orientations.

The sticking coefficients of a range of organic solutes at water surfaces are found to be more sensitive to solute structure than are the solubilities, varying by more than 10^5 while the corresponding solubilities vary by around 10^4. Moreover, there is a poor correlation between the sticking coefficients and solubilities.

The sticking coefficients at the water surface are considered in terms of the donor, acceptor, hydrophobic and steric properties of the solute.

SS1

Ultra Soft X-ray Spectroscopy for the Structure Analysis of Ions and Molecules in Solution

Hisanobu Wakita [a,b*] and Tsutomu Kurisaki [a]

[a] *Department of Chemistry, Fukuoka University, 8–19–1, Nanakuma, Jonan-ku, Fukuoka 814–0180, Japan;*
[b] *Advanced Materials Institute of Fukuoka University, 8–19–1, Nanakuma, Jonan-ku, Fukuoka 814–0180, Japan.*

Ultra-soft X-ray (50 – 1500 eV) spectroscopy is a useful tool for obtaining electronic structure information, especially, nano-level structure information of surfaces and/or light element materials. However, recent application of this tool is limited to the analysis of solid surfaces such as catalysts, semiconductors, functional metals and oxides because incident ultra-soft X-ray beam is easy to reduce its power by air or solvent of solution samples. Therefore, only a few trials have been performed to get the information of ions and molecules in solution by this spectroscopy. As the electronic structure information of solution surfaces and light elements in solution would be given by using this energy region, we have developed new spectral systems for synchrotron light and laser plasma source. Using horizontal incident ultra soft X-ray beam of synchrotron light facilities (ALS, CA and LS, Saga), we obtained the emission spectra from free surface of solution samples and the absorption spectra from the same solution samples, and analyzed their spectra using by a DV–Xα molecular orbital calculation method. We have reported the result of structure analyses for alkali metal ions, halide anions, aqueous aluminates and aluminum EDTA complexes in aqueous solution[1–3]. This review lecture shows how to measure the emission and/or absorption spectra of ultra-soft X-rays for solution samples and also the analytical results of the spectra obtained for ice & water, ions and molecules in aqueous solution.

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POSTER PRESENTATIONS

(Presenters listed in alphabetical order)

Physicochemical Properties of Mixed Sulfate Electrolyte Systems

Chandrika Akilan,* Lan-Chi Königsberger, Peter M. May and Glenn Hefter

Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia.

Mixed metal sulfate solutions are of great importance in various hydrometallurgical situations such as the extraction of nickel and cobalt from laterite ores and in the electro-refining of copper. The physicochemical properties of pure metal sulfate solutions are well known, however, little work has been done on mixed sulfate solutions even though these are of greater technological significance.

Measurements are presented on the viscosities of ternary mixtures of $CuSO_4/Na_2SO_4/H_2O$ and $MgSO_4/Na_2SO_4/H_2O$ over the whole composition range at constant total ionic strengths of 1.0 and 3.0 M at 25 °C. Densities and heat capacities of the binary and ternary mixtures of $CuSO_4$ and $MgSO_4$ with Na_2SO_4/H_2O were measured, using a vibrating tube densimeter and a Picker flow calorimeter respectively, under the same conditions. These data were used to calculate the apparent molar volumes and heat capacities of these solutions, which are compared with values predicted using Young's rule. Osmotic coefficients for these mixtures were measured isopiestically at 25 °C and the results compared with Zdanovskii's rule. Solubility measurements in the ternary systems $CuSO_4/Na_2SO_4/H_2O$ and $MgSO_4/Na_2SO_4/H_2O$ at 60 and 90 °C were measured using a solubility apparatus that permits sampling at the equilibration temperature.

Low-Frequency Raman Spectra of Supecritical Methanol

Yuko Amo,[a*] Hirotosi Abe,[a] Yasuo Kameda,[a] Usuki Takesi [a] and Yasuori Tominaga [b]

[a] *Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata* 990–8560, *Japan;*
[b] *Graduate School of Humanities and Sciences, Ochanomizu University, Bunkyo-ku Tokyo* 112–8560, *Japan.*

Hydrogen-bonded liquids, such as water and alcohols, have intermolecular vibrational mode in the region from 40 cm^{-1} to 300 cm^{-1}, because the hydrogen-bond is the origin of the restoring force between molecules. Below 40 cm^{-1}, there is a relaxation-like mode due to the collective motion of each molecule. These vibrational and relaxational modes can be observed by low-frequency Raman scattering measurements.

In general, the hydrogen-bonds among molecules become weaker with increasing temperature and decreasing density. In the supercritical state, intermolecular vibrational modes decrease and only one relaxation mode remains. The characteristic time of the relaxation mode includes the information of the molecular dynamics.

In this study, low-frequency Raman spectra of methanol have been observed from 370 K to 530 K, including the supercritical region. Raman spectra were recorded from –50 cm^{-1} to 400 cm^{-1}. The critical temperature of the methanol is 512.64 K.

Raman scattering spectra were obtained by a double grating monochromator (Jobin–Yvon U–1000). The volume of sample methanol in a pressure cell is about 1.5 cm^3. The 3 sapphire windows of 30 mm ϕ are used together with quartz backup windows for a pressure cell. The effective radius of the windows is about 15 mm ϕ.

A relaxation function based on the multiple random telegraph model(MRT model) have been applied to the reduced spectra to determine the characteristic time of the lowest frequency mode. The MRT model contains both inertia and non-white effects for rotational Brownian motion. In addition one Gaussian function and one damped harmonic oscillator are also used to fit the rest of the components in the reduced spectra.

The relaxation time first deceases with increasing temperature up to about 430 K, and then increases with increasing temperature up to 530 K. Temperature dependence of Raman relaxation time is consistent with that of dielectric relaxation time.

At 530 K, pressure dependences of the low-frequency Raman spectra have been obtained. At 14.0 MPa, there exists one relaxation mode, around 20 cm^{-1}. The second mode at 80 cm^{-1} appears with decreasing pressure. This result indicates that the new 80 cm^{-1} mode is due to collision of molecules, because the vibration mode should not exist at this temperature-pressure condition.

Structure of K[Au(CN)$_2$] in Solution: an X-ray Diffraction and Theoretical Study

Szabolcs Bálint,* Imre Bakó, Tünde Megyes, Tamás Grósz,
Tamás Radnai and Gábor Pálinkás

Chemical Research Center, Hungarian Academy of Sciences, Budapest, P.O. Box 17, H–1525, Hungary.

Structure of solvated ions in solutions has long been an attractive subject for studies by means of both experimental (spectroscopic and diffraction procedures) and theoretical (ab inito, molecular dynamics simulation) methods. However, the numerous theoretical and experimental reports still present a rather diversified picture, even for such fundamental properties as the average number of coordinating solvent molecules. Gold containing complexes are of great interest in recent decades because of their important properties, e.g. are luminescent and have a potential applicability as medicines.

X-ray diffraction experiments, ab initio calculations and molecular dynamics simulation were carried out in order to study the structure of solutions of K[Au(CN)$_2$] in various solvents (nitromethane and methanol). For molecular dynamics simulation we developed potential functions by ab initio calculations at MP2/aug-cc-pvdz/6-311+g** level. The basis aug-cc-pdzv and 6-311+g** was applied for gold and all the other elements, respectively. The basis sets were selected and tested on ionisation energies and bond interaction energies.

Beyond that, the capabilities of the methods to describe solution structure are discussed. For the studied system, the diffraction methods are performing very well in determination of intramolecular structure, but they do not give enough detailed structural information on the intermolecular structure. The results of the diffraction experiments and the results of molecular dynamics simulations are compared in order to obtain more detailed description of the solution structure using partial radial distribution functions and orientational correlation functions. Two solvent molecules are strongly coordinated to the ends of the linear complex ion. For better understanding of the nature of this arrangement we calculated the electrostatic potential painted charge density surface of the Au(CN)$_2^-$ ion. It can be seen that the whole ion is negatively charged and the electron density has a maximum at the two ends of the symmetric molecule, thus the coordinating of the solvent molecules to the cyanide ion is rather preferred in the studied solutions.

Ab-initio X-ray Absorption Spectroscopy Study of the Solvation Structure of Yttrium(III) in Dimethylsulfoxide

S. Diaz-Moreno [a]* and Jesus Chaboy [b]

[a] *Diamond Light Source Ltd, Harwell Science and Innovation Campus, Diamond House, Chilton, Didcot, Oxfordshire, OX11 0DE, UK;*
[b] *Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad de Zaragoza, Pz. San Francisco s/n, 50009, Spain.*

The solvation structure of yttrium(III) in dimethylsulfoxide has been widely studied by numerous techniques such as X-ray diffraction and absorption spectroscopy. To date, no unambiguous solution has been found and many different environments have been proposed, with coordination numbers suggested to be six, eight or nine. In this work we present EXAFS and XANES studies of the solvation structure of yttrium(III) prepared by dissolving the nitrate salt of the solvate in anhydrous dimethylsulfoxide. As the EXAFS technique was found to be limited in its ability to determine coordination numbers in this system to an accuracy no better than 20 % and furthermore, as the general sensitivity of this method to the geometric form of the local coordination polyhedra is low, we have complemented this structural investigation by a detailed XANES study. The computational analysis of the XANES structure was performed using the program CONTINUUM. This code is based on an implementation of a one-electron full-multiple scattering theory. To establish a reference state for this investigation, the solid nitrate salt of the solvate has been used as a model compound to determine the most appropriate exchange and correlation potentials for those systems. These potentials were then transferred to the analysis of the solution sample. Several possible coordination environments and conformations of the dimethylsulfoxide molecule have been investigated and the result of the XANES analysis suggests that the solvation sphere of the yttrium cation is best modelled by eight dimethylsulfoxide molecules. The angle YOS was found to be close to 130°.

Thermodynamic Properties (SLE, LLE, V^E AND H^E) of Binary and Ternary Systems of Mixtures (Alkan-1-ol, Amine, Nitrile)

Urszula Domańska-Żelazna* and Małgorzata Marciniak

Faculty of Chemistry, Warsaw University of Technology, 00–664 Warsaw, Poland.

(Solid + liquid) phase diagrams, SLE have been determined for {alkan-1-ol (octan-1-ol, or nonal-1-ol, or decan-1-ol, or undecan-1-ol) + amine (hexylamine, or octylamine, or decylamine)} binary mixtures. Solid addition compounds form with the empirical formulae 1:1.[1,2] All these compounds are congruently melting compounds. Compound formation is attributed to a strong O–H···O and N–H··· N hydrogen bonds.

SLE have been determined for {alkan-1-ol (octan-1-ol, or nonal-1-ol, or decan-1-ol, or undecan-1-ol) + 1,3-diaminopropane} mixtures. Strong cross association between the hydroxyl and the amine group ($OH \cdots NH_2$) is the dominant effect and a 2:1 congruently melting solid compound e.g. $\{(C_8H_{17}OH)_2 \cdot C_3H_{10}N_2\}$ is formed at low temperatures. Standard thermodynamic functions of the dissociation of the compound have been calculated.

SLE and LLE have been determined for {alkan-1-ol (1-octanol, or 1-nonanol, or 1-decanol, or 1-undecanol) + acetonitrile, or + propanenitrile, or + butanenitrile} mixtures and {amine + nitrile} systems.[3] Only mixtures with acetonitrile show immiscibility in the liquid phase with an upper critical solution temperature, UCST.

SLE and LLE have been determined for {nitrile (acetonitrile, or propanenitrile, or butanenitrile, or beenzonitrile) + alkan-1-ol (1-octanol, or 1-nonanol, or 1-decanol, or 1-undecanol). In the systems (acetonitrile + an alcohol) the upper critical solution temperatures, UCST were observed.

SLE have been determined for {alkan-1-ol (octan-1-ol, or nonan-1-ol, or decan-1-ol, or undecan-1-ol) + benzonitrile}[4] and for {amine (hexylamine, or octylamine, or decylamine, or 1,3-diaminopropane) + benzonitrile}.[4] Simple eutectic systems with complete immiscibility in the solid phase and complete miscibility on the liquid phase have been observed. The solubility decreases with an increase of the number of carbon atoms in the alkan-1-ol, or amine chain.

Excess molar volumes, have been determined for similar at 298.15 K and atmospheric pressure. Our experimental data of V^E_m and the literature data of H^E_m were treated in terms of ERAS model, DISQUAC and Mod. UNIFAC. DISQUAC is the only model that can be used to accurately represent excess molar enthalpies.

The basic thermodynamic properties of pure substances – the enthalpy of fusion, the difference in the solute heat capacity between the liquid and solid phase at the melting temperature, determined by the differential scanning calorimetry, DSC for alkan-1-ols and amines. The values of the enthalpies of fusion of congruently melting compounds in the binary systems (an alkan-1-ol + amine) are also presented.

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Structural Features of Concentrated Aqueous NaCl Solution in Supercritical State with Different Densities

Marina Fedotova

Institute of Solution Chemistry of Russian Academy of Sciences, Ivanovo, 153045, Russia.

Active interest in research on fluid systems based on water is caused by their large practical importance connected to the application of the unique properties of supercritical fluids in modern environmental technologies, such as supercritical water oxidation (SCWO). In particular, physical and chemical data are necessary to optimize operating conditions of SCWO reactors and the design of salt separation loops. This report discusses the structural properties of aqueous 4.37*m* NaCl solution at sub- and supercritical conditions: 1. p = 25 MPa, T = 450 – 750 K, ρ = 1.054 – 0.188 g/cm^3; 2. p = 250 MPa, T = 823 K, ρ = 0.867 g/cm^3) studied by the extended RISM integral equation method. The investigated supercritical region corresponds to technological conditions of carrying out a typical SCWO process (T = 700 – 1000 K, p = 25 MPa). It has been established that thermal ion dehydration and increasing ion association are observed in the temperature range 450–600 K. These structural changes are typical for concentrated hydrothermal solutions. The transition of the investigated system into the supercritical state is accompanied by significant reorganization in local structural fragments having H–bonds and in near-ion environments. Drastic reductions of partial coordination numbers (CN) n_{OH}, n_{NaW}, n_{ClW}, n_{NaCl} and increasing interparticle distances occur. The transformation of solution structure is observed from a state with hydrated ions and contact ion pairs (subcritical region) to a structure with non-H-bonded molecules and low-dimension clusters (supercritical region). The expected contraction of interparticle distances caused by higher compression and the expected increase of partial CN's caused by density increases are observed with increasing pressure up to 250 MPa (ρ = 0.867 g/cm^3). At T = 823 K, p = 250 MPa, each partial CN is 2–2.5 times greater than that at T = 750 K, p = 25 MPa. Comparison of the available data shows that free molecules and low molecular weight clusters should be present in low density supercritical NaCl solutions (p = 25 MPa, T = 750 K), while free molecules and larger clusters should exist in higher density supercritical NaCl solutions (p = 250 MPa, T = 823 K).

This work was supported by the Russian Foundation for Basic Research (grant No. 06–03–96317–r_centre_a).

Study of Titanium Speciation in Sulfuric Acid Solutions using Raman Spectroscopy

Fabien Baillon, Elise Provost and W. Fürst*

UCP laboratory, Ecole Nationale Supérieure de Techniques Avancées , Paris 75015, France.

Titanium oxide, because of its optical properties, is of great importance in the chemical industry, especially for pigment powder production. Precipitation by thermal hydrolysis of sulphuric solution containing titanium sulphate is a major industrial process. To improve the design process, a realistic representation of the liquid phase is necessary. However the liquid phase is a complex one and very few studies have been made of the speciation in such systems.

The aim of this work is to get experimental values that are related to the liquid phase composition in the system: water – H_2SO_4 – $TiOSO_4$. The data are obtained using Raman spectroscopy, a method already used in our laboratory to characterise speciation in strong acids solutions (nitric and phosphoric acid) over a large composition range. The measurements have been made mainly at 25 °C, the H_2SO_4 apparent concentration range being from 2 to 6 mol L^{-1}. Some experimental determinations have been made at higher temperatures to get information about the temperature effect.

When titanium is added to the sulphuric solution, a new peak appears in the RAMAN spectrum. This peak corresponds to a titano-sulphuric complex, its area being a direct function of the apparent titanium concentration. The data treatment of the peak areas allows calculation of the values of the apparent formation constant of this complex.

Use of Ion Specific Electrodes for the Determination of Salt Concentration in water / 1-butanol / NaCl System.
Modeling of the System Using an Electrolyte Equation of State

Christelle Blouet, Elise Provost and Walter Fürst*

UCP laboratory, Ecole Nationale Supérieure de Techniques Avancées, Paris 75015, France.

The salt partition coefficient is a key parameter in liquid-liquid extraction processes but its modeling is difficult because two mixed solvent systems are generally involved. The modelling implies to solve the problem of preferential solvation as well as of the choice of reference state for the ions. Furthermore, the salt concentration in the organic phase is low, making its determination difficult and leading to inconsistent published values. The system water / 1-Butanol / NaCl is very representative of this kind of systems. In the present work we have used a potentiometric method with Na^+ and Cl^- ion specific electrodes for the measurement of NaCl concentration in the 1-butanol rich phase. This method, differing from the ones used in previous papers devoted to this system, allows to discriminate between the previously published values. Values of energy of transfer ΔG_t (water / 1-butanol mixtures to water) for both homogeneous systems (aqueous phase and 1-butanol rich phase) are also deduced from the experimental potentiometric data.

The model used for the representation of data is an electrolyte equation of state combining terms from Redlich Kwong Soave equation of state as well as a MSA term for the representation of electrostatic interactions and a specific term accounting for the solvation interactions. A term allowing the use of the infinite dilution in pure water as a common reference state for the ions in the aqueous phase as well as in the organic one is also added. We have defined this term using the values of heat of transfer ΔG_t deduced from the potential experimental values.

Concentration of Carbon-PTFE Dispersion by Phase Separation

N. Furuya

Department of Applied Chemistry, Faculty of Engineering, University of Yamanashi, Takeda–4, Kofu, 400–8511, Japan.

Micro porous layer (MPL) for PEM fuel cell was prepared by dispersion of carbon black and PTFE in water containing non-ionic surfactant such as Triton X–100. Usually, this dispersion has only 13 wt% solid. The much water in the dispersion must be removed in order to obtain the thick film. However, because the PTFE particulate is agglomerated easily, the method of the shearing stress's not joining is necessary. Then, the cloud point of the surfactant property was noticed. It is well known to become hydrophobic property, when the surfactant is heated over the cloud point. The dispersion is separated to two phases of top and bottom. The upper part of the dispersion is thin, and the lower of it becomes thick. It is reported that the making process of the gas diffusion electrode using concentrated dispersion for the PEM fuel cell.

Triton X–100 (Octyl phenol ethoxylate) is used as a non-ionic surfactant with 65.5 °C as the cloud point at 1 wt% aqueous solution. The carbon black is AB–6 (Denka Black, DENKIKAGAKU KOGYO, INC.), and polytetrafluoroethylene (PTFE) dispersion (Fluon AD911, ASAHI GLASS CO., LTD). The dispersions were contained with 7.9 wt% AB–6 and 5.2 wt% PTFE in water containing the 1~30 wt% non-ionic surfactant.

The temperature of the heat treatment are 65~85°C by 0.5 to 24 hr in water bath with a temperature accuracy of +/– 0.1 °C. After heat treatment, a separated interface height of dispersion was measured. The concentrated dispersion and the surfactant were measured from the specific gravity.

The dispersion of carbon black and PTFE containing Triton X–100 was separated 2 or 3 phases at upper temperature of the cloud point of Triton X–100 – H_2O system. The dispersion is divided into upper layers with the less concentrated region of the total solid (carbon black and PTFE) and lowest layer with the more concentrated region of the total solid. Many results were separated to dilute phase and thick phase. On certain conditions, the upper layer became a clear phase. The separation rate depends on heat treatment temperature and concentration of Triton X–100 in the dispersion. It was the most quickly separated at 7 % TR dispersion. It proves that concentration dispersion with the solid (carbon black and PTFE) over 43 wt% was possible. The zeta-potential of the thin dispersion (solid contents = 13.1 %) and the thick dispersion (solid contents = 43 %) are –35mV and –34mV, respectively.The particle size of concentrated dispersion was measured. It was proven that the zeta potential and particle size of dispersion did not change by long-time heat treatment. The concentrated dispersion was stable and did not precipitate over 3 months. The concentration dispersion was suitable for the manufacture of MPL for PEM fuel cell.

Synthesis and Characterization of Trinuclear Oxo-Centered Cr(III)/Fe(III) Carboxylate Complexes: Ziegler-Natta Catalysts for Ethylene Polymerization

Aishah Mohd. Jelan [a]* and Seng Neon Gan[b]

[a] *Centre For Foundation Studies In Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia;*
[b] *Chemistry Department, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia.*

Mixed metal complexes of chromium(III) and iron(III) have been synthesized and characterized by means of elemental analysis, X-ray crystal diffraction analysis, FTIR and magnetic susceptibility measurements. Using chromatographic separations, chromium ions in the mixtures containing ferric ions were separated by using a special silica gel column functionalized with hydroxamic acid group. The chromium ion content in the eluent was determined titrimetrically. The Cr–Fe mixed metal complexes in combination with aluminium ethyl chloride were found to be active for polymerization of ethylene.

Difference in the Intermolecular Hydrogen-Bonded Structure of Aqueous Solutions Involving Amino Acid Molecules with Different Optical Activities

Yasuo Kameda,[a]* Aya Okuyama,[a] Yuko Amo,[a] Takeshi Usuki [a] and Shinji Kohara [b]

[a] *Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990–8560, Japan*
[b] *Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679–5198, Japan*

The optical activity of amino acid molecule plays an important role in various fields of chemical and biological sciences. It is well known that the solubility in water is slightly different between L- and DL-compounds. This difference in solubility may cause a difference in the hydrogen-bonded network of the solvent water molecules in highly concentrated solutions. Recently, neutron diffraction study for aqueous 2.5 mol% DL- and L-alanine solutions has revealed that the intermolecular nearest neighbor hydrogen-bonded O···H and H···H coordination number in the L-alanine solution is ca. 2 % larger than that in the DL-alanine solution.[1] The result implies that the conventional diffraction measurements can detect the difference in the intermolecular structure between solutions involving solute molecules with different optical activities. In the present study, we carried out X-ray diffraction measurements on aqueous 2.5 mol% L-, D- and DL-alanine solutions in D_2O in order to obtain information on the difference in the intermolecular hydrogen-bonded O O interaction.

Three aqueous 2.5 mol% alanine solutions in D_2O, (DL-alanine)$_{0.025}$(D_2O)$_{0.975}$, (L-alanine)$_{0.025}$(D_2O)$_{0.975}$ and (D-alanine)$_{0.025}$(D_2O)$_{0.975}$, were used. X-ray diffraction measurements were carried out at 279 K with the transmission geometry using the high-energy X-ray diffractometer installed at the BL-04B2 beam line of the SPring-8 synchrotron at JASRI, Hyogo, Japan. Incident X-ray wavelength of $\lambda = 0.202$ Å was employed in this study. Scattered intensities from the sample solution were collected in the angular range of $0.3 \leq 2\theta \leq 48.2°$ corresponding to the scattering vector magnitude of $0.16 \leq Q \leq 25.40$ Å^{-1}. Measurements were made in advance by using laboratory θ–θ type diffractometer with incident X-ray wavelength of $\lambda = 0.7107$ Å (Mo K_α) in order to check the reproducibility of the intermolecular difference function, $\Delta i^{\mathrm{inter}}(Q)$, which was derived from the difference in intermolecular interference terms among the DL-, L- and D-alanine solutions.

The $\Delta i^{\mathrm{inter}}(Q)$ functions between the DL – L and DL – D combinations exhibit small but significant interference structure, while no interference intensity was observed in the $\Delta i^{\mathrm{inter}}(Q)$ between the D – L solutions within the statistical uncertainties. $\Delta i^{\mathrm{inter}}(Q)$ functions derived from the synchrotron source and the laboratory measurements agree well with each other.

The least squares fitting analysis of the observed $\Delta i^{\mathrm{inter}}(Q)$ has revealed that the nearest neighbor difference O O coordination number Δn_{OO} and the intermolecular distance r_{OO} of the DL – L and DL – D data sets, are $\Delta n_{\mathrm{OO}} = -0.18(2)$, $r_{\mathrm{OO}} = 2.76(2)$ Å, and $\Delta n_{\mathrm{OO}} = -0.18(2)$, $r_{\mathrm{OO}} = 2.81(2)$ Å, respectively. The present results imply that the intermolecular hydrogen-bonded network in the L- and D- alanine solutions is stronger than that in the DL-alanine solution, which is in good agreement with that obtained from the previous neutron diffraction work.[1]

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The Coordination Chemistry of Solvated Metal Ions in DMPU

Daniel Lundberg* and Ingmar Persson

Swedish University of Agricultural Sciences, Box 7015, S–750 07 Uppsala, Sweden.

Studies have shown that the solvation process in DMPU is sometimes very different to those in corresponding aqueous systems. This is due to the the space-demanding properties the DMPU molecule has when coordinating to metal ions, with its two methyl groups close to the coordinating oxygen atom. The methyl groups effectively hinder/hamper the metal ion from reaching the coordination numbers present in hydrate and solvate complexes with solvent molecules with much lower spatial demands.

This work presents numerous examples of coordination number reduction, compared to the corresponding hydrates, with cadmium(II) and lutetium(III) being exceptions. Furthermore, the coordination number in solution was in several cases not the same as in the respective solid state. In solvents where five-coordinated metal ion solvates are dominating, there is an increase in the ability to form complexes, e.g. fairly strong iron(III) bromide complexes are formed in DMPU. All DMPU solvated lanthanoid(III) ions, except lutetium(III), are seven-coordinated in solution, whereas they are six-coordinated in the solid state, as well as the DMPU solvated lutetium(III) ion in solution. The DMPU solvated zinc(II) and cadmium(II) ions are fourand six-coordinated in the solid state, but both show indications of having a relatively large fraction of transient five-coordinated complexes in solution. This indicates associative and dissociative ligand exchange processes, respectively.

Measurement and Modeling of High Pressure Vapour-Liquid Equilibrium Data for Binary Systems Consisting of HFP and HFPO with Toluene, CO_2, R116 and R123

S.C. Subramoney,[a] W.M. Nelson,[a] P. Naidoo,[a*] D. Ramjugernath,[a] A. Chareton,[b] A. Valtz,[b]
C. Coquelet [b] and D. Richon [b]

[a] *Thermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu-Natal, Durban, 4041, South Africa;*
[b] *Laboratoire de Thermodynamique, Ecole Nationale Superieure des Mines de Paris, 77305 Fontainebleau, France.*

High pressure vapour-liquid equilibrium (HPVLE) data for binary systems consisting of either HFP or HFPO with toluene, carbon dioxide, hexafluroethane (R116) and dichlorotrifluoroethane (R123) were measured isothermally at 273.15 K and 313.15 K and pressures ranging up to 5.5 MPa. Two experimental methods were used for the measurements: a static synthetic method using a Pressure-Volume-Temperature (PVT) apparatus for the systems containing toluene with either HFP or HFPO and a static analytic method using the patented ROLSI™ samplers for the systems containing R116, CO_2 and R123 with either HFP or HFPO. Pure component vapour pressures for components HFP and HFPO were also measured using the static analytic apparatus over a narrow temperature range of interest. The experimental data was modelled via the direct ($\varphi-\varphi$) method using popular thermodynamic models. Such models included the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state; with the Mathias Copeman (MC) alpha function, in conjunction with the Huron Vidal (HV) and Wong Sandler (WS) mixing rules and Non-Random Two Liquid (NRTL) activity coefficient model. In general the SRK model in conjunction with the WS mixing rules correlated the experimental data the best.

Separation of Aromatic/Aliphatic Mixtures with Selected Ionic Liquids

Urszula Domańska-Żelazna and Aneta Pobudkowska*

Chemistry Department, Warsaw University of Technology, Noakowskiego 3, 00–664 Warsaw, Poland.

The design of safe and environmentally benign separation processes has an increasingly important role in the chemical industry. Ionic liquids have awakened a big interest as solvents in the last years. They show some interesting properties that would allow them to substitute classic organic solvents with improving performance and less damage to environment.

The separation of aromatic hydrocarbons (benzene, toluene, ethyl benzene and xylenes) from C_4 to C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have points in a close range and several combinations form azeotropes.[1,2,3]

In this work, we investigated the separation of benzene, *p*-xylene or ethanol from hexane by extraction with ammonium ionic liquids (butyl-(2-hydroxyethyl)-dimethylammonium tetrafluoroborate ($C_4[BF_4]$))[4], hexyl-(2-hydroxyethyl)-dimethylammonium tetrafluoroborate ($C_6[BF_4]$))[4], 1,3-dihexyloxymethyl-imidazolium tetrafluoroborate $[(C_6H_{13}OCH_2)_2IM][BF_4]$))[5]. Liquid-liquid equilibrium data were measured experimentally at 298.15 K. The experimental technique is based on direct analysis of phases at equilibrium using ^{1}H NMR, which allows quantitative analysis of the three compounds.

Use of ionic liquids as solvents for liquid extraction processes is one of their promising applications.

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A Quantum Chemistry Simulation, FTIR and Raman Spectroscopy Study of a Group of Room Temperature Ionic Liquids Based on the bis(fluorosulfonyl)imidide (FSI^-) Anion

Robert J. Rees,*[a] Adam S. Best,[a] Thomas Ruether,[a] Jewel Huang,[a] Arek Lewandowski,[a]
James Beavis,[a] Deborah Lau,[b] Anthony F. Hollenkamp,[a] Oleg Borodin [c] and Grant D. Smith [c]

[a] *CSIRO Energy Technology, Clayton South, Victoria 3169, Australia*
[b] *CSIRO Manufacturing and Materials Technology, Clayton South, Victoria 3169, Australia;*
[c] *Materials Science and Engineering University of Utah, 122 S. Central Campus Dr. Rm. 304, Salt Lake City, UT 84112 USA.*

The study of room temperature ionic liquids (RTILs) in use as electrolytes for application in high-performance energy storage devices is a topic of great current scientific and technological interest. In this study, we use quantum simulations, and infrared and Raman spectroscopy to investigate the quantum electronic structure (chemical bonding), the likely conformations and the optically induced dynamical response functions, of a particular set of RTILs based on the bis(fluorosulfonyl)imidide (FSI^-) anion. These are, N-methyl-N-propyl-pyrrolidinium ($mpPy^+$)/FSI^-, 1-ethyl-3-methyl-imidazolium ($emIm^+$)/FSI^-, and N-methyl-N-propyl-piperidinium ($mpPp^+$)/FSI^-, respectively. The $emIm^+/FSI^-$ system has, for example, been shown to have lower viscosity as a function of temperature when compared with the more commonly studied $emIm^+$/tetrafluoroborate (BF_4^-) and $emIm^+$/ bis(trifluorosulfonyl)imidide ($TFSI^-$) systems; while also indicating an equivalent and higher ionic conductivity to the $emIm^+/BF_4^-$ and $emIm^+/TFSI^-$ systems, respectively. A large cation in combination with a small anion is usually thought to result in lowering of the ionic lattice energy therefore producing a liquid phase across a large temperature range. However, the above results indicate the presence of effects, more subtle than those based on size ratios, such as: charge delocalization, charge asymmetry, and induced polarisation are influencing the phase behaviour and transport coefficients of these pure ILs over this temperature range. Here we use the quantum chemistry generated FTIR and Raman spectra and conformational geometries to isolate and analyse the key excitations in the experimental spectra. These results will be used to parameterize a quantum chemistry based Molecular Mechanics polarisable force field model, Lucretius©, in order to investigate the liquid state structure and transport properties of RTILs based on the FSI^- anion.

Interfacial Instability and Rhythmical Oscillation of Micro Phase Separation Induced by a Focused Laser

Koichiro Sadakane,* Hideki Seto and Kenichi Yoshikawa

Department of Physics, Kyoto University, Kyoto, 606–8502, Japan.

The binary mixture of water and 3-methylpyridine (3MP) is known to mix uniformly at room temperature and separate into two phases with increasing temperature.[1] Recently, we observed a micro phase separation induced by a focused laser in the one phase region: the micro-meter size droplet of 3MP was formed at the focal point. Near the critical point, an intensive fluctuation of the interface of the induced droplet was observed. In the water-rich region, the induced droplet grows and released from the focal point with the time evolution oscillatory.

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Apparent Molar Volume and Isentropic Compressibility of Tri-Sodium Citrate in Water and in Aqueous Solutions of Polyvinylpyrrolidone at $T = (283.15 \text{ to } 308.15)$ K

Rahmat Sadeghi

Department of Chemistry, University of Kurdistan, Sanandaj, Iran.

Ternary aqueous solutions of tri-sodium citrate and poly(vinylpyrrolidone) (PVP) separate into a tri-sodium citrate-rich and a PVP-rich phase over part of the composition space. Aqueous two-phase systems of this nature are useful for the separation and purification of biomaterials where the employment of a non-polar solvent/aqueous phase system would lead to degradation of biological activity.[1] Thermodynamic properties of aqueous polymer-salt systems are necessary for a fundamental understanding of the phase-forming ability and also for the development of theoretical models for the prediction of the partitioning behavior of the two-phase system. The volumetric properties of polymer or electrolyte solutions are important for understanding solute-solvent and solute-solute interactions, because they may give us an indirect insight into the conformational feature of the components in solution. In this study, precise density and sound velocity measurements have been carried out on tri-sodium citrate in aqueous solutions of 0.000, 0.002 and 0.004 m polyvinylpyrrolidone at $T = (283.15 \text{ to } 308.15)$ K at atmospheric pressure. From these experimental data, the apparent molar volume and isentropic compressibility values have been evaluated and fitted to a Redlich + Mayer type equation from which the apparent molar volume and apparent molar isentropic compressibility of the solutions at the infinite dilution have also been calculated at working temperature. The results show a positive transfer volume of tri-sodium citrate from an aqueous PVP solution to a more concentrated PVP solution. This indicates that the size of tri-sodium citrate is larger in a solution with higher PVP concentration. The apparent molar isentropic compressibility of tri-sodium citrate in aqueous PVP solutions is negative, which imply that the water molecules around the tri-sodium citrate are less compressible than the water molecules in the bulk solutions.

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Thermal Decomposition of Phenyl Diazonium Chloride in Aqueous Media at 298 K. The Role of Water and Negative Kinetic Salt Effect

G. Senanayake,*[a] P.M. Jayaweera [b] and A.S. Saputhanthri [b]

[a] *Extractive Metallurgy, Murdoch University, Murdoch, WA 6004, Australia;*
[b] *Department of Chemistry, University of Sri Jayewardenepura, Nugegoda, Sri Lanka.*

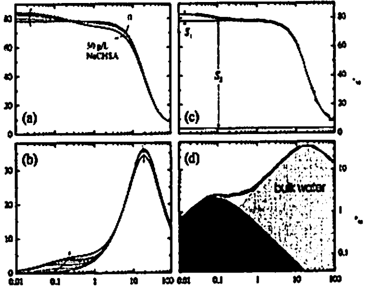
Rate constants of the decomposition of phenyl diazonium chloride (0.055 M) to phenol and nitrogen gas in aqueous solutions of sodium chloride, potassium chloride, calcium chloride, and hydrochloric acid (0 – 4 M) have been determined by measuring the volume of nitrogen evolved at 298 K. The observed negative kinetic salt effect has been analysed by considering the decrease in water activity caused by the increase in background salt or acid concentration. The first order dependence of the rate of decomposition with respect to water activity indicated that the negative kinetic salt effect is a result of the decrease in water activity.

Solvent and Solute Dispersion Processes of Aqueous Solutions of the Biopolysaccharide Chondroitin-6-Sulphate via Dielectric Relaxation Spectroscopy

Pál Sipos, [a*] Ildikó Tóth [a] and Richard Buchner [b]

[a] *University of Szeged, Department of Inorganic and Analytical Chemistry, Szeged, Hungary, H-6701 PO Box 440;*
[b] *Universität Regensburg, Institute für Physikalische und Theoretische Chemie, Germany.*

The dielectric relaxation spectroscopic (DRS) behavior of the biopolysaccharide chondroitin-6-sulphate (CHSA, the repeating dimeric unit of which will be denoted as $CHSA^{2-}$) has been studied in the $0.01 < \nu$ (GHz) < 90 frequency range. The detailed analyses of the spectra made it possible to simultaneously characterize the relaxation processes of the solute and the solvent water. On the spectra obtained for aqueous solutions of CHSA, two distinct relaxation processes appear: the one around 18 GHz corresponds to pure water, the other at ~0.2 GHz is associated with the polyion (see Figure) and – in the present case – stemming from the fluctuations of the atmospherically bound (condensed) fraction of the counterions along linear segments of the polyion.



The relaxation time of water in these solutions is equal to that of the pure water; however, its amplitude (which is proportional to the concentration of the "free" water) is significantly and systematically decreased. Thus, DRS detects only a well defined fraction of the water present, and the "missing" solvent is most likely to be irrotationally bound to the macromolecule. This effect makes it possible to quantitatively determine the effective hydration number of a repeating unit of the polyion, $Z_{ib}(CHSA^{2-})$. Such kind of information might be vital in understanding the biological role of glycosaminoglycanes, like CHSA.

The DRS spectra of aqueous CHSA solutions as a function of the polymer concentration (c_P), *p*H, temperature (*t*) and type of counterion have been determined. $Z_{ib}(CHSA^{2-})$ was found to be largely independent of c_P and the type of counterion and has the value of 18.0 ± 3.5. Addition of HCl to the solution, resulting in the partial protonation of the weakly basic ($pK_s = 3.2$) carboxylate moieties of the polymer, did not significantly alter $Z_{ib}(CHSA^{2-})$. $Z_{ib}(CHSA^{2-})$ was found to increase with decreasing temperature: at 5 °C $Z_{ib}(CHSA^{2-}) = 20$, while at 65 °C $Z_{ib}(CHSA^{2-}) = 13$ was obtained. This effect is consistent with the increasing thermal motion of the water molecules as temperature rises. The hydration number determined in the current study is significantly higher than those obtained for related other biopolysaccharides and suggests that the exceptionally abundant hydration of CHSA primarily determines its role in biochemical processes.

For the analysis of polyelectrolyte dispersion amplitudes and relaxation times, the well-known theory of Manning was followed. Depending on c_P the analysis yielded values for the average length of straight CHSA sections between 1/10 and 1/3 of the contour length (~100 nm) of the polymer. We also found, that the mobility of the condensed counterions, μ, decreases by ~40 % with the increasing concentration. Furthermore, μ is always significantly larger – between $15\mu^{\infty}(Na^{+})$ at 50 g/L and $27\mu^{\infty}(Na^{+})$ at $c \rightarrow 0$ – than the mobility of free Na^{+} ions at infinite dilution. The mechanism for such *fast and directed* ion conduction along CHS–A segments is not yet clear. Very likely, the motion of these bound but fully hydrated Na^+ counterions, which occupy on average every eighth negative charge, is highly cooperative.

Preparation of Nanocrystalline TiO_2 Photocatalysts with Controlled Rutile to Anatase Ratio from Highly Concentrated Aqueous $TiCl_4$/HCl Mixtures

Pál Sipos,* Zoltán Ambrus, Ágnes Szalai, András Dombi and Károly Mogyorósi

University of Szeged, Department of Inorganic and Analytical Chemistry, Environmental Chemistry Research Group, H–6701, Szeged, PO Box 440, Hungary.

It is well known, that the actual crystal form of TiO_2 (*i.e.*, whether it is pure rutile or anatase or the mixture of the two) strongly influences the activity of titania-based semiconductor photocatalysts. The band gap of rutile is ~3.0 eV and that of anatase is ~3.2 eV, therefore rutile has better visible light response. In spite of that, anatase is generally thought to be of better photocatalytic activity. Phase-pure titania is seldom used in heterogeneous photocatalysis, and for practical purposes utilization of anatase-rutile mixtures is much more common. It has been speculated, that a synergetic effect could exist between anatase and rutile, and their mixtures could be of better photocatalytic activity, than their phase pure forms. For example, Degussa P–25 (which might perhaps be considered as the benchmark mass produced TiO_2 photocatalyst) contains 10 – 15 m/m% rutile and 85 – 90 m/m% anatase. In our laboratories, a simple and cost-effective preparative pathway yielding nanocrystalline titania powders with controlled rutile-to-anatase ratio has been developed. The other structural parameters (particle size, particle size distribution, specific surface area and morphology) were found to be practically constant within the series of the samples prepared. This made it possible to systematically investigate the effect of phase composition on the photocatalytic performance of the products synthesized.

TiO_2 photocatalysts have been prepared from strongly acidic aqueous HCl/$TiCl_4$ mixtures with $0.1\ M \leq [HCl]_{TOT} \leq 5\ M$ and $0.05\ M \leq [TiCl_4]_{TOT} \leq 3\ M$. During the syntheses, $TiCl_4$ was added to a cold HCl solution. The initially precipitate free reaction mixture was boiled, resulting in the formation of large amount of solid, nanocrystalline (particle diameter 10 ± 5 nm) TiO_2 particles. The crystalline phases in a large number of independently prepared samples were identified from their XRD patterns. Phase pure rutile was obtained from $[HCl]_{TOT} \geq 4\ M$ $[TiCl_4]_{TOT} \geq 1.5\ M$ solutions, while pure anatase was obtained at $[HCl]_{TOT} \leq 0.1\ M$ and $[TiCl_4]_{TOT} \leq 0.1\ M$. Mixed phases were isolated from solutions of intermediate concentrations. At a given $[HCl]_{TOT}$, increasing the $[TiCl_4]_{TOT}$ resulted in gradually decreasing anatase and increasing rutile content. On the other hand, at a given $[TiCl_4]_{TOT}$ and with increasing $[HCl]_{TOT}$, the rutile content was found to systematically increase at the expense of anatase. In some samples, the presence of small amount of brookite and amorphous titania was also detected.

The photocatalytic activity was found to strongly correlate with the phase composition. In phenol decomposition the samples' photocatalytic performance gradually and significantly improves with their increasing anatase content: pure anatase samples were up to 3-times more efficient than pure rutile. In salicylic acid decomposition, unlike pure anatase, pure rutile was found to show no activity at all. Our catalysts are somewhat inferior to Degussa P–25 against both substrates, which is likely to be associated with differences between crystal size, morphology and surface properties.

pH and Ionic Strength Dependent Photocatalytic Activity of Titania in Aqueous Solutions –
Definition of Optimal Conditions for Reliably Characterizing Catalyst Activity

Pál Sipos,* Kata Demeter, András Dombi and Károly Mogyorósi

University of Szeged, Department of Inorganic and Analytical Chemistry, Environmental Chemistry Research Group, H–6701, Szeged, PO Box 440, Hungary.

The most accepted way of characterizing the efficiency (or activity) of a photocatalyst involves the measurement of the decrease of the substrate concentration in an appropriately irradiated solution in which the photocatalyst is suspended. The initial rate of substrate decomposition (r_0) is generally considered to be the measure of the "goodness" of the photocatalyst. It is well known, that r_0 is very *p*H-sensitive. This could be critical, as (i) in a system with low buffer capacity, the solution *p*H could significantly change during the test procedure; (ii) the protonation state of both the substrate and the photocatalyst might accordingly vary and (iii) their sorption interactions are expected to be *p*H-dependent too, which affect (and make ill-defined) the entire decomposition process. Further uncertainties in r_0 are likely to be associated with the ionic strength ($I = ½ \Sigma c_i z_i^2$) of the test solution. Home made photocatalysts are prone to contain significant (but at least undefined) amounts of electrolyte impurities. Their contribution to the variation in r_0 is sample dependent and the effect can only be minimized with the use of a known amount of background electrolyte. Furthermore, in practical heterogeneous photocatalytic applications, when "real life" aqueous samples (wastewater, seawater, artesian water, thermal water, etc.) are to be treated, the photocatalytic processes have to take place in an environment where I is far away from the "practically zero" value.

The vast majority of the photocatalytic activity studies published in the literature have been performed in solutions, where neither the *p*H, nor I was maintained constant, often resulting in scatters of up to ± 30 % in r_0. This experimental compromise could well be due to the fear that the components of the buffer or the supporting electrolyte could specifically interact with the surface of the photocatalyst. During our work, the use of various electrolytes and buffers in the photocatalytic decomposition of phenol test solutions was systematically investigated. Degussa P–25 titania was used as photocatalyst. From the measurements we concluded, that (i) r_0 increases systematically with the increasing pH in the $2 \leq p\text{H} \leq 7$ region; (ii) if phosphate-buffer is used, the reproducibility of r_0 significantly improves relative to non-buffered systems; (iii) when solution pH is maintained by the HCO_3^-/CO_3^{2-} buffer system, the efficiency of Degussa P–25 was found to be worse, than in analogous phosphate-containing systems, due to the radical scavenger property of the HCO_3^- and CO_3^{2-} ions; (iv) r_0 significantly increases and approaches a saturation value with I and this behavior is only slightly dependent on the type of supporting electrolyte (NaCl, KCl and Na_2SO_4).

Preliminary results indicate that similar trends are valid for substrates other than phenol (*e.g.*, salicylic acid.) From these results, for photocatalytic phenol decomposition studies in aqueous solution, we recommend the use of phosphate buffer (*p*H = 7.2) and constant ionic strength (I = 0.15 M (NaCl)). Furthermore, a simple mathematical treatment of the experimental data is also suggested which yields reliable r_0 values and resolves the dilemma, that the linear treatments of the [substrate] *vs.* time curves generally underestimate, while their exponential treatments often overestimate r_0.

Broadband Dielectric Response of Imidazolium-Based Ionic Liquids

Alexander Stoppa,[a]* Richard Buchner [a] and Glenn Hefter [b]

[a] *Institut für Physikalische und Theoretische Chemie der Universität Regensburg, 93040 Regensburg, Germany;*
[b] *Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia.*

Room-temperature Ionic Liquids (RTILs), which are formed by large organic cations with a variety of anions, are exciting new materials with actual or potential applications in many areas. The solvent properties of RTILs can be easily tuned by variation of the constituent ions. Additionally, these substances are generally non-volatile, non-flammable, thermally stable and relatively inexpensive in production. These favourable aspects have stimulated intensive research into their possible application as reaction media or for liquid-liquid extraction, with RTILs based on 1-alkyl-3-methylimidazolium cations being probably studied most.

Compared with the intense efforts in finding applications for RTILs research into the understanding of their physical properties, especially the balance of solute-solvent *vs.* solvent-solvent interactions, is lagging behind. The polarity of RTILs is a hotly debated issue with dielectric permittivity data having only recently become available, and nformation on the molecular and cooperative dynamics of these liquids is scarce. However, it is this kind of information which is needed to tailor RTILs for specific applications.

In this contribution we use dielectric relaxation spectroscopy (DRS) in the frequency range of 0.2 to 89 GHz to determine the static dielectric permittivity and the dynamical properties of imidazolium-based RTILs including [BMIM][BF_4], [BMIM][PF_6], [BMIM][DCA], [EMIM][BF_4] and [HMIM][BF_4]. This presentation will focus on the effect of cation and anion structure on RTIL dynamics, in order to unravel the complicated dielectric spectra and to elucidate the relaxation mechanisms. A characteristic of the DR spectra of apparently all RTILs – not only those based on 1-alkyl-3-methylimidazolium cations – is a broad and highly asymmetric relaxation in the MHz to low GHz region.[1,2] There are indications that this mode essentially arises from the reorientation of ions carrying a permanent dipole moment. It appears that the lifetime of the transient ion pairs perpetually formed by the collisions of the ions is insufficient to support a relaxation associated with the rotation of such species. On the other hand, similar to the recently investigated *N*-methyl-*N*-ethylpyrrolidinium dicyanamide,[3] the spectra of all investigated imidazolium-based RTILs exhibit a pronounced contribution above ~50 GHz which is probably due to the vibrations of anions and cations relative to each other.

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Structure of Hydrated, Hydrolyzed and Solvated Chromium (III) Ions in Solution

Natallia Torapava* and Ingmar Persson

Department of Chemistry, Swedish University of Agricultural Sciences, Uppsala, Sweden.

The structure of the hydrated chromium(III) ion in aqueous solution has been established for several decades. On the other hand, the coordination chemistry of the hydrolysis compounds of chromium(III) has not been studied thoroughly before, and data about chromium(III) at high pH (around 15) are inconsistent whether chromium(III) forms monomeric or polymeric species in strongly alkaline medium is an unsolved issue. Using EXAFS spectroscopy the structures of the hydrolyzed chromium(III) complexes in the pH range 2.4 – 3.8, and at pH 15 have been investigated. The EXAFS data show the presence of trimeric hydrolysis product, $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$, in the lower pH range, where each chromium coordinates six oxygens in an octahedral fashion, and with Cr–Cr distances of 2.98 and 3.57 Å, in double and single hydroxo bridges, respectively. In the pH range 4 – 12 solubility of chromium(III) oxide/ hydroxide is very low, but the solubility increases with the increasing pH. The dominating species at pH 15 is a polymeric chain structure with double hydroxo bridges, $[Cr(\mu_2{-}OH)_2(OH)_x(H_2O)_{4-x}]_n^{((1-x)+)*n}$, which precipitates with time as an amorphous solid, probably due to neutralization of the charge.

The structures of the solvated chromium(III) ion in *N,N'*-dimethylpropyleneurea (dmpu) and *N,N'*-dimethylthioformamide (dmtf) have been studied in solution by dissolution of the trifluoromethanesulfonate salt. *N,N'*-dimethylpropyleneurea is space-demanding molecule upon coordination to metal ions, often forcing the coordination number to decrease in comparison with most oxygen donor solvents. The structure of dmpu solvated chromium(III) shows a significantly shorter Cr–O bond distance, 1.92 Å, in comparison to octahedral complexes, ca. 1.96 Å, strongly indicating a five-coordinated solvate. *N,N'*-Dimethylthioformamide is sulfur donor solvent with high permittivity allowing well-solvated salts to dissociate. The structure of the dmtf solvated chromium(III) ion shows the coordination number six, with four dmtf molecules in a square plane and with trifluoromethanesulfonate oxygens in the axial positions; the Cr–S and Cr–O bond distances have been determined to 2.41 and 1.97 Å, respectively.

Complexation and Antioxidant Activity of Flavonoids with Biologically Relevant Metal Ions

Julia Torres,[a*] Paula Morales,[a] Sixto Domínguez [b] and Carlos Kremer [a]

[a] *Cátedra de Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, CC 1157, Montevideo, Uruguay;*
[b] *Departamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Canary Islands, Spain.*

Flavonoids are phenolic substances present in substantial amounts in vascular plants. Among many significant medicinal and nutritional values, antioxidant properties of flavonoids have been by far the most studied. They interact strongly with cations and experimental evidence also show that antioxidant activity is modified in the presence of metal ions. The structure-activity relationship research has been hampered to a certain extent by the lack of a full understanding of the flavonoids chemistry of interaction with biologically relevant cations. In this work we have dealt with the potentiometric study of the complexation of flavonoids (quercetin, rutin, rhamnetin and isorhamnetin) with the biologically relevant Mg^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+} in experimental conditions resembling the physiological ones (0.15 M $NaClO_4$ both at 37.0 and 25.0 °C). UV–vis spectra studies of some selected systems in methanolic solution are also included. Besides, we have measured free radical scavenging activity of the ligands and metal complexes of these systems. The results show the formation of stable species of flavonoids with these metal ions, most of them presenting 1:1 metal to ligand ratio. The flavonoids are present in these species either fully or partially deprotonated. The observed activity of methanolic mixtures of flavonoids and metal ions in equimolar amounts was always similar to that observed for the flavonoids alone in the same conditions. The unique example in which the activity is markedly increased upon addition of the metal ion is Cu–qrc. Then, when one equivalent of base was additionaly added to the 1:1 flavonoid metal mixtures, an increase in the observed antioxidant activity was observed for systems containing qrc or rha, probably due to the formation of the metal complexes upon deprotonation of the ligands. The observed activity was always higher than that showed by the corresponding flavonoid with the addition of one equivalent of base. The higher variation in this sense was observed for qrc and rha complexes of Zn and Mn.

Interaction of *myo*-inositol hexakisphosphate with Alkali and Alkaline Earth Metal Ions

Julia Torres,[a]* Nicolás Veiga,[a] Sixto Domínguez,[b] Alvaro Díaz [c] and Carlos Kremer [a]

[a] *Cátedra de Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, CC 1157, Montevideo, Uruguay;*
[b] *Departamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Canary Islands, Spain;*
[c] *Cátedra de Inmunología, Facultad de Química/Ciencias, Universidad de la República, Avenida Alfredo Navarro 3051, CP 11600, Montevideo, Uruguay.*

myo-Inositol hexakisphosphate (InsP$_6$) is a ubiquitous and abundant molecule in eukaryotic cells, whose biological functions are incompletely understood. It interacts strongly with cations, forming soluble complexes and solids, both of which are biologically relevant. Progress in InsP$_6$ biology has been delayed by the lack of a quantitative description of these interactions. In this work we have dealt with the potentiometric study of the complexation of InsP$_6$ with the biologically relevant Mg^{2+} and Ca^{2+} both in experimental conditions resembling the physiological ones (0.15 M $NaClO_4$, 37.0 °C) and also using a non interactive medium (0.15 M NMe_4Cl). We have also extended this study to Sr^{2+} and Ba^{2+}, which behave similarly to Mg^{2+} and Ca^{2+}, but giving even less soluble systems. We have also studied the interactions with Li^+, Na^+ and K^+. Results show that cation charge has a major influence on the strength of interaction: while the monovalent ions interact very weakly even at high pH, the divalent cations are bound by InsP$_6$ to a considerable extent at neutral pH, and almost completely bound at high pH. Within the alkali metals, variations in log K values are only slight. The comparison among the alkaline earth metal ions shows that at low pH values, only Mg^{2+} exhibits significant binding, mostly as $[Mg(H_6L)]^{4-}$; the remaining cations remain essentially free in this pH region, because they form complexes only with more deprotonated forms of InsP$_6$. At physiological pH values (7.4), all the alkaline earth metal ions show considerable interaction with InsP$_6$ (at a L:M^{2+} ratio of 1.5) with less than 30 % of metal remaining free. At this point, the extent of interaction follows the order Mg~Ba>Sr>Ca; the presence of soluble pentametallic species, $[M_5(H_2L)]$, in the cases of Mg, Ba and Sr but not in that of Ca, contributes to this trend. Finally, the compounds $[M_5(H_2L)]\cdot nH_2O$ (n = 22 for Mg and 16 for Ca, Sr and Ba) were synthesised, characterized, and their solubilities were measured to ensure a complete description of these systems.

Excess Molar Volumes of Binary Liquid Mixtures of (Water + Amines) at Several Temperatures and Atmospheric Pressures

Ricardo Belchior Tôrres* and Pablo Andres Riveros Munoz

Departamento de Engenharia Química, Centro Universitário da FEI, 09850–091, São Bernardo do Campo, São Paulo, Brasil.

As a continuation of our study of volumetric properties of binary mixtures containing water[1], in this work, excess molar volumes $\left(V_{\mathrm{m}}^{\mathrm{E}}\right)$ of water + propylamine, or + n-butylamine, or + s-butylamine, or + diethylamine, or + t-butylamine have been determined as a function of composition at different temperatures and atmospheric pressure. The temperatures studied were 283.15, 288.15, 293.15, 298.15 and 303.15 K. Excess molar volumes were determine from the densities of pure liquids and mixtures using a vibrating-tube densimeter manufactured by Anton Paar (Model DMA 4500). The systems exhibit negative $V_{\mathrm{m}}^{\mathrm{E}}$ values over the entire composition range in the temperature range studied. The experimental $V_{\mathrm{m}}^{\mathrm{E}}$ decrease in the sequence: n-butylamine < propylamine < s-butylamine < diethylamine < t-butylamine. The experimental results are discussed.

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The authors wish to thank the financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Project FAPESP Nº 04/11855–8. P.A.R. Munoz thanks also FEI for the award of the scholarship PBIC 17/06.

Excess Molar Volumes of Binary Liquid Mixtures of (Dichloromethane + Amines) at Several Temperatures and Atmospheric Pressures

Ricardo Belchior Tôrres* and Heloísa Emi Hoga

Departamento de Engenharia Química, Centro Universitário da FEI, 09850–091, São Bernardo do Campo, São Paulo, Brasil.

As a continuation of our experimental and theoretical studies of volumetric properties of binary mixtures containing chloroalkanes[1,2], in this work, excess molar volumes $\left(V_{\mathrm{m}}^{\mathrm{E}}\right)$ of dichloromethane + n-butylamine, or + s-butylamine, or + diethylamine, have been determined as a function of composition at different temperatures and atmospheric pressure. The temperatures studied were 288.15, 293.15, 298.15 and 303.15 K. The excess molar volumes were determined from the densities of the pure liquids and mixtures using a vibrating-tube densimeter manufactured by Anton Paar (Model DMA 4500). Excess molar volumes representation is sigmoid in the temperature range studied and the $V_{\mathrm{m}}^{\mathrm{E}}$ values are small in absolute value. The experimental results are discussed.

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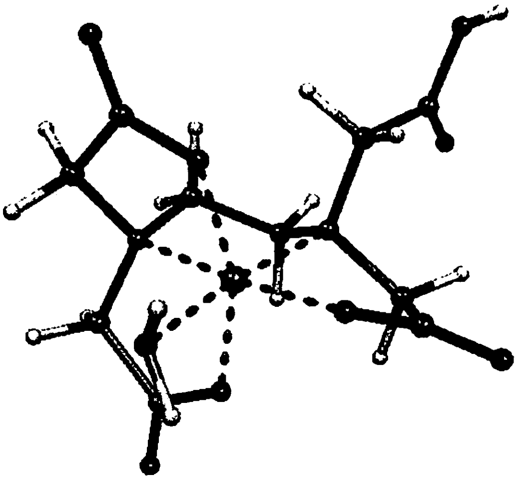
Study of the Intra-Molecular Rearrangement of Aluminium(III)–Edta by NMR and DFT Calculations

Mihály Purgel,[a] Imre Pápai,[b] Róbert Jószai [a] and Imre Tóth [a*]

[a] *Department of Inorganic and Analytical Chemistry, University of Debrecen, H–4010 Debrecen, Hungary;*

[b] *Chemical Research Center of the Hungarian Academy of Sciences, Budapest, Hungary.*

Multinuclear NMR studies of Al(edta)$^-$ complex by ^{1}H, ^{13}C and ^{27}Al NMR in solution while varying the temperature, pH or using different solvents have been done. The features of the high field NMR spectra show that the complex has similar structure in solution and solid state, i.e. the Al(III) are octahedrally coordinated by the hexadentate edta ligand. The fluxional rearrangement of the chelate rings can be followed by ^{1}H and ^{13}C NMR spectroscopy. We have determined the rate constants and the activation parameters for these two (coupled) intra-molecular rearrangements in dmso-water mixture. The turning of ethylene group is faster ($\Delta H^\# = 33.1 \pm 2.8$ kJ mol^{-1}, $\Delta S^\# = -110 \pm 10$ J mol^{-1} K^{-1}, a $\log k_{298} = 1.30 \pm 0.48$) compared to the *exchange* between the *axial* and *equatorial* acetate arms ($\Delta H^\# = 60 \pm 4$ kJ mol^{-1}, $\Delta S^\# = -25 \pm 21$ J mol^{-1} K^{-1}, $\log k_{298} = 0.9 \pm 0.3$).



Density functional theory (DFT) calculations have been carried out to reveal the effect of protonation and the role of solvent. The exchange between the *axial* and *equatorial* acetate arms of Al(edta)$^-$ is more favourable via protonation of an acetate arm. The suggested mechanism consists of six elementary steps, namely *the protonation and dissociation of the acetate group, deformation of the chelate rings* involving the acetate groups, the *turning of an ethylene group, re-coordination of the acetate arms* followed by *the deprotonation* in a back and forth movement. In fact this *indirect exchange* means interconversion of the two enantiomers of the complex. (This process does not involve the complete dissociation of an imino-diacetate group required for the fast inversion of the N-donor in a *direct exchange*). The calculated energy values of the intermediates are in the same order of magnitude as the energy of hydrogen bonds in aqueous solution. The calculations with one water molecule in the inner coordination sphere indicate further stabilization of the dissociated intermediate species. Calculations have also been done for a hydroxo-complex, Al(edta)(OH)$^{2-}$, which may result in different mechanism.

The work was supported by the OTKA K63388 research grant.

On the Conformation of *N*-alkyl-*N*-methylpyrrolidinium Bis-(trifluoromethanesulfonyl) Imide Room Temperature Ionic Liquids: DFT Calculations and Raman Spectroscopic Study

Yasuhiro Umebayashi,[a]* Takao Fujimori,[a] Shuhei Fukuda,[a] Kenta Fujii,[b] Ryo Kanzaki,[a]
Munetaka Takeuchi [a,c] and Shin-Ichi Ishiguro [a]

[a] *Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, 812–8581, Japan;*
[b] *Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga 840–8502, Japan;*
[c] *FUJITSU LIMITED, Chiba 261–8588, Japan*

Conformational behavior of ions in the liquid state is one of the topics among recent physicochemical fundamental studies on the Room Temperature Ionic Liquids. Raman spectra of *N*-alkyl-*N*-methylpyrrolidinium bis-(trifluoromethanesulfonyl) imide ($P_{1n}{}^{+}Tf_2N^{-}$; $n = 3$ and 4) ionic liquids were recorded at 298 K over the wide frequency range, and DFT calculations for the cations were performed. The $P_{14}{}^{+}$ ion gives various types of conformations with respect to the pyrrolidinium ring and *N*-butyl group. DFT calculations indicate that, among others, the *eq*- and *ax*-envelope conformers with the *N*-butyl group at *equatorial* and *axial* positions, respectively, against planar 4 carbon atoms of the envelope pyrrolidinium ring ($-NCH_2CH_2CH_2CH_2-$) are relatively stable, and the former gives the global minimum. It revealed by comparing observed and calculated Raman spectra that the *eq*- and *ax*-envelope conformers are present in equilibrium in the $P_{14}{}^{+}Tf_2N^{-}$ ionic liquid, while, interestingly, the $P_{14}{}^{+}$ ion is present mainly as the *ax*-envelope conformer in the $P_{14}{}^{+}Br^{-}$ crystal. The presence of conformational equilibrium of the $P_{14}{}^{+}$ ion in the liquid state is further supported by Raman spectra measured by varying temperature. It is also established that conformation of the *N*-butyl group is restricted to the *trans*-TT, in which the butyl group locates *trans* against its nearest carbon atom in the pyrrolidinium ring, and all carbon atoms in the butyl chain are located all *trans* each other.

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Electrical Conductivity Measurements of Process Fluids Using Re-entrant Microwave Resonators

Chaitanya Vangala,[a]* Andrew Rafty,[a] Eric F. May [a] and Peter M. May [b]

[a] Centre for Petroleum and Energy Research, School of Mechanical Engineering, University of Western Australia, Crawley WA 6009 Australia;
[b] School of Chemical and Mathematical Sciences, Murdoch University, Murdoch WA 6150 Australia.

The electrical conductivity of fluids used in extractive metallurgy is a key property for fundamental models of these fluids and for on-line process monitoring. Unfortunately, conventional methods of measuring conductivity are often inapplicable to these process fluids because their conductivity is too high and/or they are incompatible with the temperature and pressure requirements. We are developing a new method of measuring the electrical conductivity of these fluids at elevated temperatures using microwave re-entrant cavities. Such devices have been used very successfully to measure the complex dielectric permittivities of non-polar[1], polar and weakly conducting[2] fluids at high-pressures and temperatures. The high-degree of electric and magnetic field separation in re-entrant cavity resonances means that these instruments can in principle be used to distinguish between conductivity and absorption losses. Such information could improve, for example, complementary techniques for dielectric relaxation spectroscopy. However, previous efforts to measure concentrated solutions have been unsuccessful because the fluid's high-conductivity destroyed the cavity's resonance[3].

We have constructed a gold-plated re-entrant cavity with a resonance frequency of 170 MHz and a half-width of 0.08 MHz. When the cavity was partially filled with 15 mL of de-ionised water (7×10^{-4} S/m) the resonance half-width was unchanged; however, when filled with 15 mL of 5 M KOH (≈ 85 S/m) the resonance half-width increased to 1.73 MHz. Importantly, despite the solution's high conductivity, it was still possible to measure the resonance. It should thus be possible to extend the technique to high temperature operation. Future work will focus on improved electrical modelling to relate solution conductivity to the measured resonance frequency and half-width.

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Ion Association and Hydration in Aqueous Solutions of LiCl and Li_2SO_4

Wolfgang Wachter,[a]* Šarka Fernandez,[a] Richard Buchner [a] and Glenn Hefter [b]

[a] *Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg, Germany;*
[b] *Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia.*

The behaviour of Li^+ in aqueous solutions is strongly influenced by its very large energy of solvation. Given the strong affinity of Li^+ for water molecules, it is not surprising that many simple lithium salts crystallise as hydrates and that the anhydrous salts are often very hygroscopic. However, in marked contrast to the other alkali metal ions, especially Na^+ and K^+, solutions of Li^+ salts have received limited attention. This is surprising given their physiological activity: Li^+ salts are used for the treatment of manic-depressive psychoses, the first such drug to be recognised. As Birch points out in his recent review,[1] the physicochemical properties determining the action of Li^+ on the human organism are not well understood, but are certainly less complex than those of organic drugs. Thus, understanding the physicochemical properties of $Li^+(aq)$ may be of particular value in the understanding of fundamental processes in drug-receptor interactions.

Dielectric relaxation spectroscopy (DRS), which measures the response of a sample to an applied electromagnetic field in the microwave region, is a powerful technique for the study of ion-ion and ion-solvent interactions. Complex permittivity spectra obtained as a function of the field frequency provide unique insights into the nature and dynamics of electrolyte solutions. This work presents a dielectric relaxation study of aqueous solutions of LiCl and Li_2SO_4 at 25 °C and over a wide range of frequencies ($0.2 \leq \nu/\mathrm{GHz} \leq 89$) . These salts were chosen as typical representatives of 1:1 and 1:2 lithium electrolytes with potentially very different behaviour in aqueous solution.

However, the present results for these two Li^+ salts share many similar characteristics. Thus, the spectra of both salts were best described by a superposition of four Debye processes, consisting of two water relaxations at ca. 8 and 0.5 ps and two ion-pair contributions at ca. 200 and 20 ps, corresponding to the presence of double-solvent-separated (2SIP) and solvent-shared (SIP) ion pairs. Consistent with spectroscopic studies no contact ion pairs were detected. The overall ion association constants K°_A obtained were in good agreement with literature data for both salts. Detailed analysis of the solvent relaxations indicated that Li^+ has a significant second solvation sheath although there was some discrepancy between the hydration numbers obtained from the two salts, which might arise from competition for the solvent from the anions.

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Solubility Determinations in the Systems $CaSO_4$–MSO_4–H_2O (M = Mg, Mn, Co, Ni, Cu, Zn) for Derivation of Thermodynamic Characteristics of Ion Interactions $Ca^{2+} - M^{2+} - SO_4^{2-}$

G. Wollmann* and W. Voigt

Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, 09596 Freiberg, Germany.

Experimental data suited for the derivation of thermodynamic quantities of $CaSO_4$ in mixed sulfate solutions of bi- or trivalent metal ions are very scarce, particularly for high sulfate concentrations. Methods like isopiestic measurements or electrochemical cells with calcium-selective electrodes are not applicable for conditions of low calcium and high MSO_4 concentrations. Solubility studies can provide such data if the thermodynamic solubility constant of the solid phase is known with sufficient accuracy, equilibration is not fast enough and formation of solid solutions can be excluded. Crystallization of gypsum, $CaSO_4 \cdot 2H_2O$, full-fills these requirements in the solutions of interest. Therefore, the solubility of gypsum in the systems $CaSO_4$–MSO_4–H_2O (M = Mg, Mn, Co, Ni, Cu, Zn) have been determined over a wide concentration range by an isothermal saturation method at $T = 25$ °C and 40 °C. In order to ensure highest possible accuracy, special dilution and calibration procedures for calcium concentration determination by means of ICP were applied. With increasing molality of the heavy metal sulfate the solubility of gypsum decreases first and then rises to a maximum. This phenomenon can be seen at both temperatures. The comparison with literature data revealed a main lack in solubility data of the determined systems.

From the solubility data the mean ionic activity coefficient $\gamma_\pm(CaSO_4)$ was calculated as a function of the MSO_4-concentration. At low concentrations of MSO_4 all data fall onto one line. Only above 0.5 mol/kg H_2O the individuality of the bivalent metal ions becomes pronounced, for the solubility data as well as for the mean ionic activity coefficient $\gamma_\pm(CaSO_4)$. For an understanding of the differentiation between the systems thermodynamic and transport characteristics have been compiled, and brought into relation with the mean ionic activity coefficient $\gamma_\pm(CaSO_4)$ in dependence on concentration of MSO_4.

The tendencies are discussed in terms of electrostatic interactions, hydration and ion pairing competition of the bivalent metal salts MSO_4 and $CaSO_4$.

Kinetics of L-alanine Oxidation by Potassium Permanganate

Karim Zare [a,b*] and Farrokh Gharib [a]

[a] *Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran;*
[b] *Chemistry Department, Islamic Azad University, Science & Research Campus, Tehran, Hesarak, Iran.*

In this research the oxidation of L-alanine by potassium permanganate and its conversion to aldehyde in highly acidic medium was studied by UV–vis spectrophotometric technique. Concentrations of L-alanine, potassium permanganate, acid and manganese dioxide as a catalyst have been changed and the observed rate constants have been determined. Temperature dependence of the reaction rates were studied and activation parameters were determined according to the Arrhenius and Eyring equations. Finally two different mechanisms were proposed for the catalyzed and uncatalyzed oxidation of L-alanine by potassium permanganate.[1–2]

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