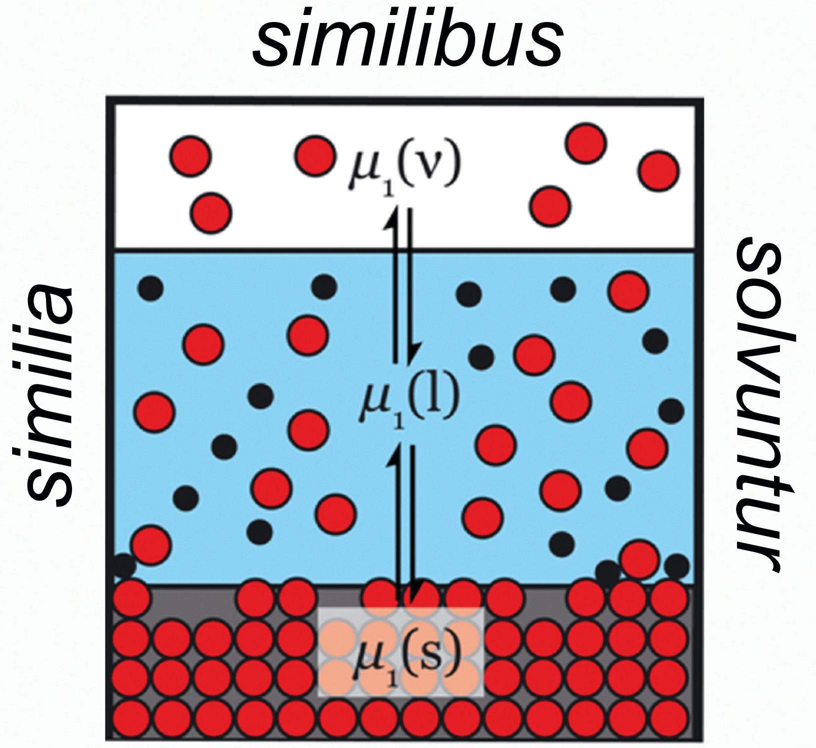
ISSP 17

24-29 JULY 2016

GENEVA

17TH INTERNATIONAL SYMPOSIUM ON SOLUBILITY PHENOMENA AND RELATED EQUILIBRIUM PROCESSES



ABSTRACT VOLUME

Preface

The International Symposium on Solubility Phenomena and Related Equilibrium Processes (ISSP) is a well-established biennial conference. For six days, ISSP 17 will bring together scientists with a shared interest in solubility. Solubility-related processes are of fundamental importance in a large number of scientific disciplines and practical applications, ranging from ore processing and nuclear waste disposal to the use of medicines and the transport of pollutants. The main subjects of the conference will include, but not be limited to: aqueous solutions at high ionic strength, biomineralisation, computer assisted modelling (*ab initio*, molecular dynamics and Monte Carlo as well as equilibrium and kinetic calculations), gas-liquid solubility, ionic liquids, molten salts, solid solutions, solubility and nanoparticles.

ISSP17 will include two applied workshops focusing on highly topical issues. A workshop on Solubility in energy and waste issues of emerging concern will discuss greenhouse gases (carbon capture and storage), emerging energy technologies (fracking, geothermal energy) and long-term behaviour of waste disposal sites. A workshop on Technology-critical elements prone to hydrolysis in biological and environmental systems will deal with less-studied elements that are increasingly being used in new technologies in the fields of communication, mobility and green energy.

The University of Geneva is honoured to host ISSP 17 from 24 to 29 July 2016. Geneva enjoys a long scientific tradition, with figures such as Jean-Charles Galissard de Marignac, who measured the atomic mass of 28 chemical elements, discovered one, ytterbium, and co-discovered another one, gadolinium. It is home to CERN, one of the world's largest centres for scientific research, as well as to over 300 international and non-governmental organisations and permanent missions. The organisers wish all participants a pleasant stay in this multicultural, thrilling environment.

Montserrat Filella & Wolfgang Hummel
Geneva, July 2016

Previous conferences

2014	ISSP16	Karlsruhe, Germany
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1992	ISSP5	Moscow, Russia
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1984	ISSP1	London, ON, Canada

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Microbes as geologic agents in the sedimentary equation

Judith McKenzie, Crisogono Vasconcelos

Geological Institute, ETH Zurich, Switzerland

e-mail: judy.mckenzie@erdw.ethz.ch

The application of thermodynamic principles provides valuable insight into the geochemical processes promoting authigenic precipitation of sedimentary minerals in natural environments. Although chemical thermodynamics is firmly established as a predictor of the equilibrium conditions for mineral stability, it has not always proven possible to successfully transfer these conditions into the laboratory to study specific mineral formation. An example of this conundrum is the carbonate mineral dolomite [$CaMg(CO_3)_2$], which commonly occurs throughout the geologic record but is rarely found forming in modern environments. Furthermore, it has proven difficult, if not impossible, to precipitate dolomite in the laboratory under low-temperature sedimentary conditions.

Déodat de Dolomieu, a French geologist (1750-1801), is credited with defining dolomite as a discrete carbonate mineral because it did not effervesce with weak hydrochloric acid. He published his observations in the "Journal de Physique" in 1791, and, as a result, the mineral, as well as the rock and the scenic southern Tyrolean Mountains, bear his name. In the intervening 225 years, the chemo-physical conditions required to precipitate stoichiometric dolomite under Earth surface conditions have been extensively explored, but experimental precipitation remained elusive. Beginning in the mid-1950's, a number of modern dolomite precipitating environments were discovered and studied, but it still remained impossible to replicate the chemical equilibrium conditions needed to precipitate dolomite in the laboratory. Although geochemical evidence of *in situ* microbial metabolism indicated that microbes might play a role, it has only been in recent years that a microbial factor promoting dolomite precipitation has been successfully tested and evaluated in controlled culture experiments.

The role of microbes in mineral precipitation is not restricted to carbonates but is apparently involved in the precipitation of numerous other so-called bio-minerals, such as clays, phosphates, etc. Recently, a growing field of research, known as geomicrobiology, spotlights the interface between biology and geology under sedimentary conditions. Indeed, studies at this new frontier provide an innovative approach to understand Earth's history. The resulting assessment of biogeochemical phenomena holds great promise of revealing new insights into the co-evolution of life and minerals, as revealed in the Earth's 3.5-billion-year sedimentary rock record. Additionally, the study of natural environments combined with laboratory experiments and evaluation of geologic samples can provide important data relevant for the exploration of possible life on extra-terrestrial planets.

OC 1

Internally consistent thermodynamic data for hydrothermal mineral solubility equilibria in the system Ca-Mg-Na-K-Al-Si-O-H-C-Cl

George Dan Miron[1,3], Thomas Wagner[2], Dmitrii A. Kulik[3], Christoph A. Heinrich[1]

[1]Institute of Geochemistry and Petrology, ETH Zurich, Switzerland
[2]Department of Geosciences and Geography, University of Helsinki, Finland
[3]Laboratory for Waste Management, Paul Scherrer Institut, Switzerland

e-mail: dan.miron@psi.ch

The quality of solubility calculations relies on the robustness of thermodynamic models and on the accuracy and internal consistency of the thermodynamic dataset. The standard state Gibbs energies of aqueous ions and complexes were simultaneously refined against a large selection of critically evaluated experimental data on mineral solubility, covering the entire Ca-Mg-Na-K-Al-Si-O-H-C-Cl system **over** wide ranges in temperature and pressure. The procedure was done using the revised Helgeson-Kirkham-Flowers equation of state and the extended Debye-Hückel activity coefficient model [1]. Thermodynamic properties of solubility-controlling minerals were adopted from the dataset of Holland and Powell (2002; Thermocalc dataset ds55) [2] which was assumed to be fully internally consistent and non-adjustable. Results from new high-precision conductance and potentiometric experiments on electrolyte association were used to derive more reliable and accurate equilibrium constants for weak complexation and to constrain the properties of complexes which are insensitive to the solubility data. The global optimization of standard Gibbs energies of aqueous species $G^{o}_{1,298}$ at 1 bar 25 C was performed with the GEMSFITS code [3]. The optimization procedure was set up in such a way that the speciation equilibria for ion pairs and complexes are always maintained. These complexes and ion pairs were constrained to the freely optimized parameters through the independently derived reaction constants.

Application of our consistency-improving strategies and tools in the Ca-Mg-Na-K-Al-Si-O-H-C-Cl system results in equal distribution of errors over the pressure, temperature and compositional space; yields confidence intervals for the optimized parameters; and permits straightforward repetition of fitting procedures when the new or improved experimental data become available. Simultaneous fitting in the composition – P – T space, including the explicit uncertainty calculations presented in this study, provides a clear guide to future experimentation, by highlighting the most sensitive gaps in fluid-mineral phase equilibria experiments. The dataset reproduces all available fluid-mineral phase equilibria and mineral solubility data with good accuracy over a wide range in temperature, pressure and composition.

Due to the constraints used in the optimization procedure, the only way to resolve the existing discrepancies present in the fluid-mineral equilibria experiments, needed for achieving internal consistency, is to make unavoidable changes to the $G^{o}_{1,298}$ values of some freely adjusted ions. For maintaining the agreement with different available thermodynamic data frameworks (e.g. CODATA), the change in $G^{o}_{1,298}$ for these aqueous ions was added with the opposite sign to the respective mineral form the Holland and Powell database, thus preserving all mineral solubilities. The new dataset can be successfully used to model complex multi-component, multi-phase chemical systems, including mineral solubility and aqueous speciation, at the levels of confidence and accuracy that was not possible before.

References

[1] H.C. Helgeson, D.H. Kirkham, G.C. Flowers, *Amer. J. Sci.* **281**, 1249-1516 (1981).
[2] T.J.B. Holland, R. Powell, *J. Metam. Geol.* **16**, 309-343 (1998).
[3] G.D. Miron, D.A. Kulik, S.V. Dmytrieva, T. Wagner, *Appl. Geochem.* **55**, 28-45 (2015).

Acknowledgements

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OC 2

Remarks on the evaluation of complexation constants of cations with the sulfate anion

Glenn Hefter[1], Cezary Gumiński[2]

[1]Department of Chemistry, Murdoch University, Perth, WA 6150, Australia
[2]Department of Chemistry, University of Warsaw, 02093 Warsaw, Poland

e-mail: cegie@chem.uw.edu.pl

This work is being carried out as a service to the scientific community under the auspices of the IUPAC Sub-committee on Solubility and Equilibrium Data. It is the first step in performing a critical evaluation of the thermodynamic data (including stability constants, enthalpies, entropies, heat capacities and volume changes) for proton- and metal-sulfate equilibria in aqueous solution. Such data are spread widely throughout the scientific literature and compiling them fully is a significant task.

Sulfuric acid is a major industrial commodity with a vast range of applications: in the production of chemicals, metallurgy, geochemical extraction and so on. While sulfuric acid is usually described in textbooks as a strong, diprotic acid, this is only true in very dilute solutions. At the concentrations typically used in most practical applications the protonation of the sulfate ion: $H^+(aq) + SO_4^{2-}(aq) \Leftrightarrow HSO_4^-(aq)$ lies well to the right and it is in essence a 1:1 electrolyte. Modelling the chemical speciation in acidic sulfate solutions therefore clearly requires accurate knowledge of the equilibrium constant (K_a) for the above reaction. While this constant has been well characterized in dilute solutions for over a century, its magnitude in the presence of other electrolytes, and under non-standard conditions of temperature and pressure, is less well known. For this reason it is timely to collect and to make a critical evaluation of the existing data for this equilibrium.

The equilibrium results related to the formation of complexes (or ion pairs) of metallic cations with sulfate anion are collected and assessed in the similar way. These complexes are of moderate or weak stability. All the relevant data are collected in form of tables similar to previous data bases but the assemblage is much more scrupulous and extensive. The experimental methods used for the determinations of the equilibrium constants and other properties are compared.

The selected complexation constants may be correlated with a cation valency, its form in aqueous solution (hydrated or oxy-cations) and its position in the periodic table of elements.

OC 3

The NEA thermochemical database project: 30 years of accomplishments

Maria-Eleni Ragoussi, Davide Costa

Nuclear Energy Agency (NEA), Organisation for Economic Co-operation and Development (OECD)
46, quai Alphonse Le Gallo, 92100 Boulogne-Billancourt, France

e-mail: davide.costa@oecd.org

The OECD NEA Thermochemical Database Project (TDB) was initiated in 1984 with the aim of creating a database of chemical thermodynamic values that would fill significant gaps in radionuclide chemistry and support the modelling requirements for performance assessments of radioactive waste disposal systems [1]. The preparation of this database follows strict guidelines [2] to assure the high quality, consistency, reliability and CODATA-compatibility of the data provided. The projects, undertaken by TDB in five Phases, have continuously been supported by the participating organizations (mostly national nuclear waste authorities and institutions) through a well-structured organization. This poster will describe the concept and scientific principles of the TDB project, together with accomplishments and current developments. Thirteen volumes of the *Chemical Thermodynamics Series* have so far been published and a great number of selected values have populated the electronic database, treating the most significant elements related to nuclear waste management and becoming an international reference in the field. The work carried out has resulted in the publication of major reviews on the chemical thermodynamics of inorganic species and compounds of U, Np, Pu, Am, Tc, Ni, Se, Zr, Th, Sn and Fe and on simple organic complexes of U, Np, Pu, Am, Tc, Ni, Se, and Zr with citrate, oxalate, EDTA and iso-saccharinic acid, as well as the publication of a state-of-the-art report on solid solutions of interest in nuclear waste management [3]. Currently, work is focused on the completion of four reviews: Iron (2nd volume), molybdenum, ancillary data and the 2nd update of the actinides and technetium volumes, in addition to two state-of-the-art reports on thermodynamic considerations for cement minerals and on high ionic strength systems.

References

[1] M.-E. Ragoussi, S. Brassinnes, The NEA Thermochemical Database Project: 30 Years of Accomplishments. *Radiochim. Acta*, **103**, 679 (2015).
[2] OECD NEA, *TDB-0–TDB-6, TDB project guidelines* (2013). http://www.oecd-nea.org/dbtdb/guidelines/
[3] OECD NEA, *Thermochemical Database (TDB) Project Publications - Chemical Thermodynamics Series* (2013). http://www.oecd-nea.org/dbtdb/info/publications/

OC 4

Heat capacities and entropies of molybdates and carbonates

Ernst Gamsjäger[1], Heinz Gamsjäger[2]

[1]Institut für Mechanik, Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria
[2]Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria

e-mail: e.gamsjaeger@unileoben.ac.at

Immobilizing nuclear waste as borosilicate glasses can result in the detrimental formation of yellow phases. Sodium and calcium molybdates are host crystals for these yellow phases. It is thus of both scientific and ecological interest to investigate the thermodynamic properties of alkali and alkaline earth metal molybdates. The most reliable standard molar entropies of solid phases are calculated from calorimetrically determined low-temperature heat capacity values. In the case of alkaline earth metal molybdates these data had been measured until very recently only for $MgMoO_4$ (cr) and $CaMoO_4$, powellite, at $T > 50$ K. Consequently extrapolation of the heat capacity function to $T = 0$ K played and still plays an important role. In contrast to the classical trial and error approach, integrals with integral boundaries as fitting parameters should be included in the nonlinear fit of experimental data resulting in the adjustable parameters of analytical functions. This paper compares classical and recently developed methods to evaluate data for $SrMoO_4$, $CaMoO_4$ and $MgMoO_4$ by state of the art mathematical routines. In addition, the thermodynamic properties of $PbMoO_4$ (wulfenite) and $PbCO_3$ (cerussite) are investigated by a similar procedure.

OC 5

Quaternary ammonium-based deep eutectic solvents

Mónia A. R. Martins[1,2], Liliana P. Silva[1,3], Paula V. A. Pontes[2], Guilherme J. Máximo[2], Olga Ferreira[3], Simão P. Pinho[3], Eduardo A. C. Batista[2], Antonio J. A. Meirelles[2], João A. P. Coutinho[1]

[1]CICECO, Departamento de Química, Universidade de Aveiro, Portugal
[2]EXTRAE – FEA, Universidade de Campinas, Brazil
[3]Associate Laboratory LSRE-LCM, Instituto Politécnico de Bragança, Portugal

e-mail: spinho@ipb.pt

With the growing focus in green chemistry, researchers are increasingly seeking environmentally friendly solvents. Recently, a new class of eco-friendly solvents has been proposed, the Deep Eutectic Solvents (DES). These are mixtures of two, or more compounds, formed by hydrogen bond complexation, for which the eutectic point is far below to that of an ideal liquid mixture. DES can be easily prepared by mixing the components at a moderate temperature, without chemical reactions and complex purification steps. Many are prepared using cheap and well-characterized biodegradable materials, making the "synthesis" green and safe. They may also be classified as designer solvents since their structures can be adjusted by selecting the hydrogen-bond donor–acceptor combinations, tailoring their phase behavior and physical properties. The most common components used in DES formulations are quaternary ammonium salts, particularly choline chloride, due to its non-toxicity, biodegradability and economic synthesis.

While much work has been reported using these novel solvents, the number of DES which are liquid at room temperature is still very limited. Moreover, data on their phase diagrams are surprisingly scarce despite the important information they can provide on the donor-acceptor interactions, and the range of compositions and temperatures for operating these systems. The aim of this work is thus to characterize and analyze phase diagrams of DES composed by $[N_{1111}]Cl$, $[N_{2222}]Cl$, $[N_{3333}]Cl$, $[N_{4444}]Cl$, and [Ch]Cl with carboxylic acids, in the whole composition range. Differential scanning calorimetry and a visual observation method were used to determine the phase transitions and built the liquidus line. Results allow an interpretation about the non-ideality of the liquid phase, and the strength of the hydrogen bond donor-acceptor interactions. Additionally, a number of systems with eutectic points below 298.15 K were found, showing that those solvents can be used at room temperature.

Workshop

Technology-critical elements prone to hydrolysis in biological and environmental systems

Introduction

Montserrat Filella

Institute F.-A. Forel, University of Geneva, Switzerland

e-mail: montserrat.filella@unige.ch

New technologies in the fields of communication, mobility and energy drive the increasing extraction, use and emission of a range of trace elements, including platinum group metals, certain rare earth elements, and Y, Nb, Ta, Ga, In, Tl, Ge and Te. Due to limited resources and supplies, most of these elements are considered technology-critical elements (TCE) of strategic importance, and initiatives at national and international levels are therefore underway to secure their availability in the coming years. Because of their increasing use, poorly understood biogeochemical behaviour and (potential) toxicity, TCE and other rare trace elements are emerging inorganic contaminants of substantial concern. Solubility, equilibrium and kinetic processes concerning TCEs sensitive to hydrolysis are the object of this workshop.

Invited lecture

Learning from Ascidians about trafficking of hydrolysis-prone metals

Ann Valentine

Temple University, USA

e-mail: ann.valentine@temple.edu

Organisms require several metal ions that are prone to hydrolysis and hydrolytic precipitation in an aerobic aqueous environment, and they are exposed to many more. Iron is the best-studied example; it is required by nearly every species but precipitates as an insoluble Fe(III) oxide. Many forms of life exert exquisite biological control over inorganic coordination chemistry to cope with this problem of metal management. In 1911, Henze reported remarkably high vanadium concentrations in the blood cells of a marine invertebrate chordate, the ascidian. Over the past one hundred years, the ascidians were established as masters of the biological chemistry of very hydrolysis-prone metals, with various ascidian species accumulating high concentrations of iron, vanadium, and titanium, among others. These three metals have very different histories of biological relevance, and many questions remain about how, and ultimately why, these organisms sequester them. This talk will address the aqueous coordination chemistry that organisms like ascidians must control if they are to manipulate hydrolysis-prone metal ions, and describes some of the ascidian biomolecules that have been implicated. The ascidians have much to teach us about how to manage metals like iron, titanium, and vanadium and about how that ability evolved.

OC 6

Speciation and electrochemistry of indium in aqueous sulfate and chloride solutions

Charlotte Ashworth, Gero Frisch

TU Bergakademie Freiberg, Institut für Anorganische Chemie, Leipziger Straße 29, 09599 Freiberg

e-mail: charlotte.ashworth@chemie.tu-freiberg.de

Indium is considered a strategically important element due to its increasing use in electronic components [1-2] and the worldwide demand for indium is expected to increase dramatically in the near future [3-4]. A greater understanding of the speciation of indium formed in solution is essential for explaining electrochemical behaviour and determining the equilibrium constants required for optimising the design of extraction methods.

In this study we have used differential pulsed voltammetry (DPV) to determine the half wave potential ($E_{1/2}$) of indium reduction in aqueous chloride and sulfate solutions of varying ligand concentration. Assuming the general indium reduction mechanism in equation 1, by plotting $E_{1/2}$ against the logarithm of the respective ligand concentrations, the number, x, of ligands, L, bound to an In^{3+} ion can be estimated from the linear gradient.

$$[\mathrm{InL}_x]^{(3+nx)} + 3\ \mathrm{e}^- \rightleftharpoons \mathrm{In} + x\ \mathrm{L}^n \tag{1}$$

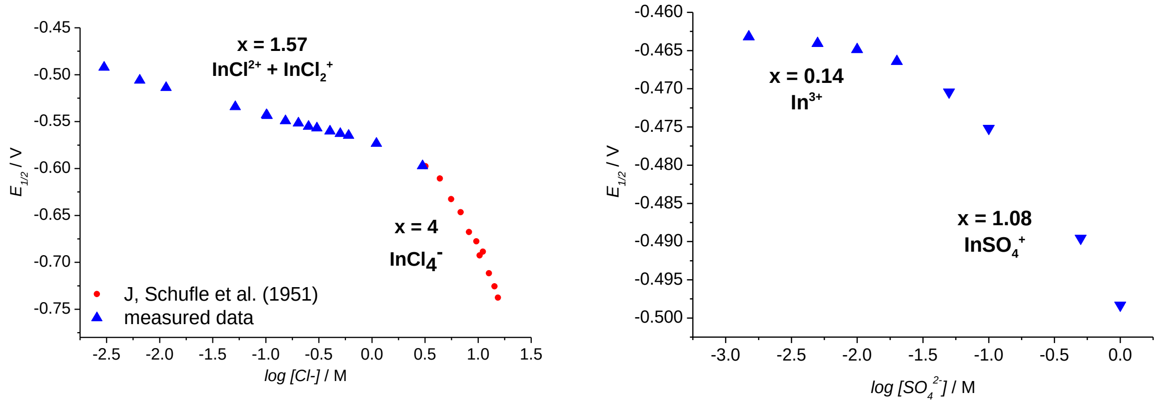

Fig 1: Nernstian plots of $E_{1/2}$ of In^{3+} reduction with respect to (l) chloride and (r) sulfate ion concentration, where x = the number of ligands bound to an In^{3+} ion in solution.

In a solution with a chloride concentration below 3 M, the electrochemically active species are $InCl^{2+}$ and $InCl_2^+$ resulting in an average chloride coordination number of 1.5. At higher chloride concentrations the chloride coordination is 4 and the speciation is therefore $InCl_4^-$.

In a solution with low sulfate concentration the coordination number is almost 0, we assume speciation in this range is almost completely the hydrated In^{3+} ion. At a higher sulfate concentration, $InSO_4^+$ is the electrochemically significant species in solution and therefore the sulfate coordination number is 1. All the aforementioned speciation is consistent with our results produced from the geochemical modelling program PHREEQC.

Further investigations will concentrate on methanesulfonate [5] and other ligands [6] which are discussed as potential electrolytes for electrowinning and –refining.

References:

[1] V.S. Saji, *J. Korean Electrochem. Soc.* **14**, 6170 (2011).
[2] V.S. Saji, *Solar Energy* **85**, 2666 (2011).
[3] C. Kim, *Renew. Sust. Energ. Rev.* **13**, 493 (2009).
[4] S. White, *Crit. Rev. Env. Sci Tech.* **42**, 155 (2012).
[5] F. Walsh, *Surf. Coat. Tech.* **259**, 676 (2014).
[6] M. Lee, *Scand. J. Metall.* **33**, 279 (2004).

Invited lecture

Technology-critical elements Ga, In and La in medical inorganic chemistry

Chris Orvig

Medicinal Inorganic Chemistry Group, Department of Chemistry and Faculty of Pharmaceutical Sciences,
University of British Columbia, Vancouver BC, Canada

e-mail: orvig@chem.ubc.ca

The role of metal complexes and ligands as therapeutic and diagnostic agents is burgeoning because of medicinal chemistry's broadening interest in elements from across the Periodic Table; the current annual value of medicinal inorganic chemistry is USD $\$10^9$-$10^{10}$. *Cis*-platin, one success, is the archetypal inorganic drug - it contains not one atom of carbon. Principles in the design of metal compounds or ligands as drugs will be discussed in detail with examples from work in the speaker's research laboratories presented as illustration. These examples are taken from recent work with a particular focus on the technology-critical elements Ga, In and La in diagnostic and therapeutic radiopharmaceuticals, and antibiotic and antiosteoporosis compounds.

Reference

K.D. Mjos, C. Orvig. Metallodrugs in medicinal inorganic chemistry. *Chem. Rev.* **114**, 4540-4563 (2014).

OC 7

Can we predict the behaviour of prone-to-hydrolysis TCEs in aqueous media of analytical, toxicological or environmental significance?

Montserrat Filella[1], Marc Biver[2], Guillaume Jiranek[1], Juan-Carlos Rodríguez-Murillo[3], Yves Schulze[1]

[1]Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland
[2]Bibliothèque Nationale de Luxembourg, 31 Boulevard Konrad Adenauer, L-1115Luxembourg, Luxembourg
[3]Museo Nacional de Ciencias Naturales, CSIC, Serrano 115 dpdo., E-28006 Madrid, Spain

e-mail: montserrat.filella@unige.ch

A number of trace elements that until recently were only considered to be laboratory curiosities have now become essential components in a variety of applications ranging from information to 'green energy' related technologies. The current strategic importance of these elements is such that they have now been labelled as 'energy-critical elements' or 'technology-critical elements' (TCEs). The TCE tag is a geopolitical and economical one, not based on any scientific criteria. For this reason, elements with very different chemical characteristics are found under the TCE umbrella. Most, but not all of them, are present at very low concentrations in the upper crust and in environmental compartments. Some have rarely been used in the past but there are exceptions (e.g., Pt, Gd). Some are prone to hydrolysis and relatively insoluble. Moreover, the list of elements considered as TCEs is variable, depending on the source. Among TCEs prone to hydrolysis, Nb, Ta, Ga, In, Ge and the Rare Earth Elements are always present in TCE lists. They are the object of this communication.

The degree of the current knowledge on their environmental fate and (eco)toxicity is very low. In a first step, aspects to be considered include:

(i) Compiling and analysing existing environmental data (Can we measure them? Are their concentrations increasing? Do they behave conservatively?).

(ii) Developing new analytical methods when needed.

(iii) Compiling and evaluating published equilibrium constants and identifying gaps.

(iv) Evaluating the role of natural organic matter in their solubility (following the iron example…).

(v) Clarifying their kinetics of ligand exchange at neutral pH values.

(vi) Predicting their speciation in culture media.

The current situation, work in progress and challenges involved in future research will be discussed.

Keynote lecture

Gas solubility in ionic liquids: progress and prospects

Johan Jacquemin

School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK

e-mail: johan.jacquemin@qub.ac.uk

Since the last two decades, the determination of the gas solubility in ionic liquids has attracted the attention of various research groups. Several data are now available, in the literature, for various (gas(es) + ionic liquid) combinations, as well as, for different (temperature and pressure) conditions. However, such data were determined by various research groups using different experimental techniques and ionic liquid batches, which may affect the overall accuracy of published data, as well as, related thermodynamic functions and general conclusions. During this talk, the current state of information on experimental data, existing models, solvation mechanisms and properties will be summarized and discussed to highlight progress made so far, general tendencies and efforts still requested.

Keywords: Ionic Liquids, Gas Solubility, Temperature, Pressure, Experimental Data, and Modeling.

OC 8

Solubility parameters of room temperature ionic liquids and solubilities in them

Yizhak Marcus

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

e-mail: yizhak.marcus@mail.huji.ac.il

Many room temperature ionic liquids (RTILs) have found practical applications as ‘green’ solvents for a variety of solutes and their mixtures for their extraction, separation, purification, and reaction. Key quantities for such applications are the solubilities of the reactants and products in the RTILs. Their prediction from the properties of the RTIL solvents and the prospective solutes is a desirable goal. The Hildebrand solubility parameters are used for this purpose for organic solvents. The question arises whether these are useful for RTIL solvents too?

The Hildebrand solubility parameters, δ_{HR}, of RTILs (subscript $_{\mathrm{R}}$) are obtained from their molar cohesive energies, i.e., molar enthalpies of vaporization and molar volumes as:

$$\delta_{\mathrm{HR}} = [(\Delta_{\mathrm{V}}H_{\mathrm{R}} - RT)/V_{\mathrm{R}}]^{1/2} \qquad (1)$$

The mole fraction solubilities of solutes (subscript $_{\mathrm{S}}$) should be obtained from regular solution theory (provided it is applicable) as:

$$\ln x_{\mathrm{S(R)}} = -(V_{\mathrm{S}}/RT)(\delta_{\mathrm{HR}} - \delta_{\mathrm{HS}})^2 \qquad (2)$$

The infinite dilution activity coefficients, $\gamma_{\mathrm{S(R)}}{}^{\infty}$, are obtained for volatile organic solutes from gas chromatography measurements. However, since for them $\ln x_{\mathrm{S(R)}} = -\ln \gamma_{\mathrm{S(R)}}{}^{\infty}$, the derived expression (2) does *not* hold. This is due to neglect of polar and hydrogen-bonding interactions and discrepancies in the molecular sizes of solute and solvent that the regular solution theory ignores.

Much better agreement is obtained for gaseous solutes, foremost for carbon dioxide, the absorption of which by RTILs is of considerable environmental interest. In fact an *empirical* expression:

$$\ln H_{\mathrm{S(R)}} = a + b(\delta_{\mathrm{HR}} - \delta_{\mathrm{HS}})^2 \qquad (3)$$

where $H_{\mathrm{S(R)}} = p_{\mathrm{S}}/x_{\mathrm{S(R)}}$ is Henry’s law parameter at a partial pressure p_{S} of the solute gas, is applicable. Therefore knowledge of the δ_{HR} of RTILs to be used for the absorption of carbon dioxide (for which $\delta_{\mathrm{HS}} = 17.9\ \mathrm{MPa}^{1/2}$) is still significant.

It turns out that the cohesive energy densities of RTILs, $\delta_{\mathrm{HR}}{}^2$, are inversely proportional to their molar volumes, estimated without knowledge of the molar enthalpies of vaporization:

$$\delta_{\mathrm{HR}}{}^2/\mathrm{MPa} = (1.48\underline{+}0.21)\mathrm{x}10^5/(V_{\mathrm{R}}/\mathrm{cm}^3\mathrm{mol}^{-1}) \qquad (4)$$

OC 9

CO_2 absorption in ionic liquids under high-pressure conditions

Takashi Makino[1], Tatsuya Umecky[2], Masaki Watanabe[3], Daisuke Kodama[3],
Mitsuhiro Kanakubo[1]

[1]Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Japan
[2] Graduate School of Science and Engineering, Saga University, Japan
[3]Department of Chemical Biology and Applied Chemistry, College of Engineering, Nihon University, Japan

e-mail: makino.t@aist.go.jp, m-kanakubo@aist.go.jp

Ionic liquids (ILs) are salts, of which the melting temperatures are at or below ambient temperature. They have some unique characteristics such as non-volatility, non-flammability, high electrical conductivity, miscibility with various chemicals, and so on. Furthermore, CO_2 is dissolved well in some kinds of ILs, while ILs are not evaporated at all in the CO_2 phase even under the high-pressure conditions. These favorable characters can overcome some drawbacks of the current CO_2 absorbents, flammability and volatility of absorbents, and high energy-consumption during absorption and/or desorption. Since the first report on the phase behavior of the IL + CO_2 system [1], CO_2 absorption in ILs has been well-investigated at various temperatures and pressures to develop better IL absorbents and design CO_2 capture processes using ILs. However, the mole fraction scaled solubilities and the Henry constatns were only reported in many cases. They are measures of the CO_2 absorption properties in ILs, but the molecular volumes/weights of ILs are not taken into consideration. More important information for the engineering design in the CO_2 separation is the CO_2 capacity, i.e. the molarity or molality scaled solubilities of CO_2. A very limited information is available for the effect of chemical modifications on the CO_2 capacities in ILs. Our research group have investigated pressure–volume–temperature–composition (*pVTx*) relations for IL + CO_2 mixtures to obtain both the mole fraction and molarity scaled solubilities [2]. For example, we demonstrated that the ether group on the ammonium enhanced the molarity of CO_2 through the interaction between the cation and CO_2. Here, we summarize our earlier and recent studies on the CO_2 absorption behaviors in the physical and chemical IL absorbents under high pressure conditions. For the physical absorbents, the cations were imidazoliums, phosphoniums, ammoniums, and amidiniums, and the anions were amides, borates, sulfates, and sulfonates. The chemical absorbents were the carboxylate and amino acid salts with the dialkylimidazolium and tetraalkylphosphonium cations. We discuss the effect of chemical modifications on the CO_2 physisorptions and chemisorptions based on the *pVTx* relations and the derived thermodynamic parameters of solution.

References

[1] L.A. Blanchard *et al.*, *Nature* **399**, 28-29 (1999).
[2] For example, D. Kodama *et al.*, *J. Supercrit. Fluids* **52**, 189-192 (2010); T. Makino *et al.*, *Fluid Phase Equilib.* **357**, 64-70 (2013); T. Makino *et al.*, *Fluid Phase Equilib.* **362**, 300-306 (2014); T. Makino *et al.*, *J. Chem. Eng. Data* **59**, 1435-1440 (2014); M. Kanakubo *et al.*, *ACS Sustainable Chem. Eng.* **4**, 525-535 (2016).

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OC 10

Microemulsification of hydrophobic ionic liquid to enhance enzyme solubility and catalytic performance

Xirong Huang, Wenjuan Zhang

School of Chemistry and Chemical Engineering, Shandong University, P R China

e-mail: xrhuang@sdu.edu.cn

Room temperature ionic liquids (ILs) are molten salts at room temperature or below 100 °C. They are composed of organic cations and inorganic/organic anions. ILs have many advantages such as low volatility, high stability, good miscibility with organic compounds and unique component designability. Compared to traditional organic solvents, ILs are usually considered as "green" solvents. In 2000, Erbeldinger *et al.* released the first report on the enzyme catalysis in ILs. Since then, many endeavours have been devoted at home and abroad to the studies on enzyme catalysis in ILs.

Previous studies indicate that an enzyme usually has catalytic activity in ILs if the enzyme is active in an organic solvent. Also it has been found that the catalytic performance of enzymes in ILs is correlated with the hydrophilicity/hydrophobicity of ILs. In hydrophobic ILs, such as [Bmim][PF_6] and [Bmim][NTf_2], enzymes are not soluble, and usually their powders are suspended in ILs. The suspended enzymes exhibit catalytic activity and even good stability, but only small portions are available for catalysis due to their poor dispersion. By contrast, in hydrophilic ILs, enzymes are soluble, but their activity is poor due to the unfavourable interaction between enzymes and ILs. It follows that the major problem for the utilization of ILs as media for enzyme catalysis is how to reconcile the contradiction between the maintenance of the enzyme activity and the solubility of the enzyme in ILs.

The functionalization of ILs is the most direct and effective strategy to resolve the contradiction. The designability of ILs makes it possible to seek compatible ILs which could dissolve as well as stabilize enzymes. However, little progress has been made in this area. The lack of detailed knowledge of the structure-property correlation of ILs and the enzyme-IL interaction mechanism should be responsible for the stagnancy. Although the immobilized enzyme can be dispersed at a molecular level, it is still difficult to avoid the direct interaction of ILs with the enzyme. Therefore, changing the microenvironment surrounding the enzyme to improve the catalytic performance is also a good strategy.

Reviewing the evolution of the medium engineering for enzyme catalysis, we get a good enlightenment. For hydrophobic ILs (HILs), a good solution to the problem is to create a microenvironment suitable for the dispersion of an enzyme as well as the maintenance of the enzyme activity by dispersing water into HILs; i.e., the so-called microemulsification of HILs with surfactants. The microemulsification results in larger surface area than in the HIL/water two-phase system and makes the reactions of hydrophobic substrates with a hydrophilic enzyme go easily. Moreover, the formed water pool can restrict the change of the conformation of the enzyme. Studies have shown that most enzymes can maintain their catalytic activity and stability in HIL-based microemulsions. In this talk, we make a brief description of the recent progress made in my group in the enzyme catalysis in HIL-based microemulsion. The emphasis is put on the phase behavior and the microstructure of HIL/H_2O/surfactant ternary system and the effect of the microstructure on the catalytic performance of the enzyme encapsulated in HIL-based microemulsion.

Keywords: enzyme catalysis, hydrophobic ionic liquids, microstructure, phase behavior, surfactants.

OC 11

Partition coefficients octanol-water of selected (–)-menthol-substituted chiral ionic liquids

Adéla Andresová[1], Joanna Feder-Kubis[2], Markéta Florianová [3], Barbara Basarabová[3], Kateřina Čubová[3], Zdeněk Wagner[1], Magdalena Bendová[1]

[1]E. Hála Laboratory of Separation Processes, Institute of Chemical Process Fundamentals of the CAS,
v. v. i. Rozvojová 2/135, CZ-16502 Prague 6, Czech Republic
[2]Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
[3]Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Břehová 7, 115 19 Prague 1, Czech Republic

e-mail: bendova@icpf.cas.cz

Natural substances obtained from plants, such as terpenes, appear to be suitable precursors in synthesis of greener ionic liquids. Menthol seems to be one of the mostly reported terpene substituent occurring in ionic liquids; it is an abundant, cheap (~€60/kg), nontoxic, and environmentally friendly material. For instance, alkylimidazolium based chiral ionic liquids (CILs) with a natural (1R,2S,5R)-(–)-menthol substituent, viz. 3-alkyl-1-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chlorides were found to show an application potential through their antimicrobial and antielectrostatic activity. It is therefore important, among others, to evaluate the potential environmental risks by studying their (eco)toxicity and tendency towards bioaccumulation.

Octanol-water partition coefficients, log P, may be considered as one of the indicators for the tendency to bioaccumulation. For this reason, log P was measured as a function of the alkyl chain length on the cation for selected species of the above-mentioned chiral ionic liquid series. The data were processed by means of mathematical gnostics to evaluate the relationship between the structure of the studied ionic liquids and log P.

OC 12

Structure-property relationships and the impact of impurities on the physico-chemical properties for novel oligoglyme-substituted ionic liquids

Jan Rotrekl

E. Hála Laboratory of Separation Processes, Institute of Chemical Process Fundamentals of the CAS,
v. v. i. Rozvojová 2/135, CZ-16502 Prague 6, Czech Republic

e-mail: rotrekl@icpf.cas.cz

Ionic liquids (ILs) represent a group of organic salts with an enormous variability in chemical structure and physico-chemical properties and consequently with a broad application potential. The aim of this work is to establish relationships between the chemical structure and physico-chemical properties of the studied Ils and to identify the influence of coloured impurities on these properties. These two points form an essential base for any application of these materials. The knowledge of the influence of impurities is a crucial factor for a proper characterization of ILs and should be inherent to any study of ILs, as will be shown.

In a previous study [1] addressing the physico-chemical properties of 1-butyl-3-alkyl-imidazolium bis{(trifluoro-methyl)sulfonyl}imides (abbr. bistriflate), where alkyl is a pentyl, isopentyl, or cyclopentyl, a strong influence of the isomerization of the studied ILs was found, allowing for a fine-tuning of their properties. In the present work, the butyl substituent was replaced by 2-(2-ethoxyethoxy)ethyl and a similar range of 1-(2-(2-ethoxyethoxy)ethyl)-3-alkyl-imidazolium bistriflates was prepared. The introduction of an (oligo)ether group was choosen with regard to a possible electrochemical application, as this substituent can significantly improve the IL conductivity.

To characterize the new chemical species presented in this work, several properties of pure substances were determined as a function of temperature. The isobaric heat capacities were measured using a differential scanning calorimeter μDSC III by Setaram. The density and speed of sound were measured using a vibrating tube densitometer, the viscosity was measured using a Stabinger viscometer, both apparatuses by Anton Paar. Electrical conductivity were measured using a WTW TetraCon 325 conductivity cell.

All the ILs were synthesized in house. Some of them, however, were yellow to brown immediately after the synthesis, although they should be colourless. The problem of colour is well known and is usually solved by two approaches. At best the ILs are decolorized by means of active carbon and/or alumina column chromatography. Very often, though, the colour is ignored and it is assumed it has no impact on the IL properties. The origin of these impurities is little known and it is presumed it comes from the IL precursors. In this work the properties were found to vary significantly at every decolorization step. For this reason emphasis was put also on identifying these impurities.

References

[1] A. Andresová, J. Storch, M. Traïkia, Z. Wagner, M. Bendová, P. Husson, Branched and cyclic alkyl groups in imidazolium-based ionic liquids: Molecular organization and physico-chemical properties. *Fluid Phase Equilib.* **371**, 41-49 (2014).

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OC 13

Impact of the size and shape of ions on the ability of ionic liquids to dissolve cellulose

Xianqgian Meng[1,2], Julien Devemy[1,2], Pascale Husson[1,2], Arnaud Gautier[1,2],
Jean-Michel Andanson[1,2]

[1]Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France
[2]CNRS, UMR 6296, ICCF, F-63178 Aubière, France

e-mail: j-michel.andanson@univ-bpclermont.fr

Cellulose is the most abundant natural polymer on earth and one of the major components of biomass. Natural cellulose is a partially crystalline biopolymer with numerous H-bonds in between the polymers chains which make this material especially stable. For the current industrial processes as well as for the future ones, greener processes to dissolve cellulose must be found: solvents fully recyclable and processes which are efficient energetically. Some ionic liquids are good solvents for cellulose dissolution. Ionic liquids are only composed of ions and it exist millions of anion – cation combinations. Unfortunately, it is not yet possible to predict which ionic liquids will be the most efficient to dissolve cellulose. Studies of ionic liquids have shown in many cases that the addition of a molecular co-solvent (DMSO, for example) improves the ability of ionic liquids to dissolve cellulose [1,2]. Ionic liquids are viscous and the dissolution of high amounts of a polymer like cellulose makes them even more viscous. The kinetic of the dissolution of cellulose in ionic liquids can then be a limiting factor for the dissolution. Being able to understand how the transport properties and the molecular interactions are limiting the dissolution will help to design new ionic liquids.

In this work, our objective is to understand how the size and shape of the anion and cation can affect the dissolution of cellulose in ionic liquids and ionic media (ionic liquid + co-solvent). We have synthesized a set of new ionic liquids based on tetra-alkyl-ammonium cation and carboxylate anion since some of these ionic liquids are capable to dissolve cellulose [3]. We have tested the ability of these new ionic liquids to dissolve cellulose using polarized optical microscopy [1]. Molecular dynamic simulations of cellulose microfibril (few nanometers in diameter, representative of natural cellulose) in ionic media has also been developed in order to observe the structure of the solvent around the cellulose [4]. Ionic liquids with different anions and cations are then compare in order to explain how the size and shape of the ions can perturb the dissolution of cellulose.

References

[1] J.-M. Andanson *et al., Green Chem.* **16**, 2528 (2014).
[2] J.-M. Andanson *et al., Chem. Commun.* **51**, 4485 (2015).
[3] F. Boissou *et al., Green Chem.* **16**, 2463 (2014).
[4] S. Velioglu *et al., J. Phys. Chem. B* **118**, 14860 (2014).

OC 14

Temperature dependent hydration behavior of chemically modified celluloses in aqueous solution

Toshiyuki Shikata, Kengo Arai

Division of Natural Resources and Eco-materials, Graduate School of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

e-mail: shikata@cc.tuat.ac.jp

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1. Introduction: Cellulose is one of the most abundant natural resources generated by plants every year. However, its industrial applications are highly restricted because of its insolubility into most of common solvents including water. To solve this serious problem, many kinds of chemically modified celluloses have been supplied. In this study, we pay attention to methylated and hydroxypropylated cellulose ether (ChMC) which possesses high solubility in cold water, but loses it at temperature higher than e.g. 50 ºC. The reason for the temperature dependent solubility in water should be related to the temperature dependence of its hydration number. Here, we report the hydration numbers of ChMC samples in aqueous solution as functions of temperature determined using broadband dielectric spectroscopic techniques.

2. Experimental: Series of water soluble ChMC samples were kindly supplied by Shin-Etsu Chemical Co., Ltd. (Tokyo), which have the substitution numbers for methyl and hydroxypropyl groups of 1.9 and 0.25, respectively, for 3 hydroxy groups in each glucose unit and have the weight average molecular weights: $M_w = 20\times10^3$, 75×10^3 and 300×10^3. The ChMC samples were dissolved into pure water at concentrations up to c ~0.4 M in repeating units.

A network analyzer N5230 (Agilent, Santa Clara) was used for dielectric measurements over a frequency range from $\omega = 3.14\times10^8 - 3.14\times10^{11}$ s^{-1}. In a lower frequency range from $\omega = 6.28\times10^6 - 1.88\times10^{10}$ s^{-1}, an RF LCR meter 4287A (Agilent) was operated. Dielectric measurements were performed in a temperature range from T = 10 ºC to a clouding point (phase transition temperature) for each sample solution. The real and imaginary parts (ε' and ε'') of the electric permittivity were determined using the standard way.

3. Results and Discussion: Dielectric spectra for all the aqueous solution of ChMCs were perfectly decomposed into three kinds of Debye-type relaxation modes over the temperature range measured. The relaxation strength of the fastest process, ε_1, assigned to the rotational relaxation mode of free water molecules in solution decreased in proportion to the concentration, c. Because the value of ε_1 indicates the amount of free water molecules, how many water molecules hydrate to a glucose unit (n_H, the hydration number) was determined from the dependence of ε_1 on c at each temperature. The determined n_H value for each ChMC sample is shown in Fig. 1 as a function of temperature, T. The fact that the n_H values were independent of M_w reveals that the n_H value represents the local information at a monomeric glucose size in ChMC samples with M_w higher than a certain value. An arrow seen in Fig.1 represents a clouding point for the ChMC samples, which was independent of M_w in the examined range. Remarkable dehydration behavior was observed with increasing T irrespective of M_w. Moreover, it seems that there is a critical hydration number of ~5.0 for ChMC samples to be dissolved into water. In aqueous solutions of ChMC samples with different substitution numbers, the dependence of n_H on T altered from that observed in Fig. 1 substantially depending on the substitution number.

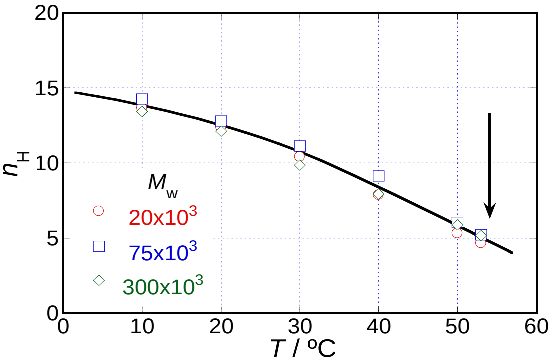

Fig. 1: Dependencies of hydration numbers, n_H, for the ChMC samples at various M_w.

Workshop

Solubility in energy and waste issues of emerging concern

Introduction

Wolfgang Hummel

Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

e-mail: wolfgang.hummel@psi.ch

Solubility and equilibrium related processes are called to play a key role in emerging society subjects such as greenhouse gases (carbon capture and storage), emerging energy technologies (fracking; geothermal energy) and long-term behaviour of waste disposal sites.

The objective of this workshop is to gather experts on these topics and to ask them to elucidate the state-of-the-art in their fields, what data are needed (with some specific examples) and whether these data are available.

This overview could trigger future SSED projects motivated by the societal need of well-reviewed data sets to be applied in these fields of emerging concern.

Invited lecture

Fluid-rock interactions related to unconventional shale gas produced water and drilling waste

Rosemary Capo

Department of Geology and Planetary Science, University of Pittsburgh, USA

e-mail: rcapo@pitt.edu

The expanded application of horizontal drilling and hydraulic fracturing technologies for unconventional oil and gas production from organic rich black shales, such as the Marcellus Shale in the Appalachian Basin, USA, has resulted in a dramatic increase in hydrocarbon production from low permeability reservoirs, new insights into the geochemical evolution of formation fluids high in total dissolved solids (TDS), and emerging environmental challenges related to the disposal of produced water and drilling waste that can contain heavy metals and naturally occurring radioactive material (NORM).

Disposal of flowback and produced waters from unconventional wells with generally high ionic strength fluids (TDS content sometimes $>2\times10^5$ mg/L) is a significant environmental issue. The median TDS concentration of Na-CL brines from Marcellus Shale gas wells is 1.6×10^5 mg/L, with barium (Ba) content $>2\times10^4$ mg/L and strontium (Sr) content over 10^4 mg/L. The uranium-rich shale results in elevated radium concentrations in the produced water that can exceed 6×10^3 pCi/L. Another emerging issue of concern is the environmentally safe disposal of drilling waste from hydraulically fractured horizontal wells that can extend more than a kilometer into the target formation (usually black shale). A single lateral leg can produce more than 300,000 kg of drilling material, and organic rich black shales have elevated concentrations of heavy metals and NORM. For example, in the Marcellus Shale, Ba, Sr, arsenic content can be as high as 3300, 300, and 90 mg/kg, respectively, and U concentrations over 45 mg/kg have been reported. Trace metals can potentially be either solubilized or immobilized under different landfill conditions.

The geochemical evolution of formation brines and the fate and transport of trace metals in drilling waste reflect mineral reservoirs and fluid-rock processes including mineral dissolution, sorption, complexation and cation exchange. Sequential extraction experiments provide insight into specific reservoirs that affect trace element mobility (water soluble salts, exchangeable cations, and carbonate and silicate mineral reactions). Natural isotopic tracer studies (e.g. ^{87}Sr/^{86}Sr; ^{7}Li/^{6}Li) can record stages of formation fluid evolution as seawater-dominated fluids are altered by carbonate and clay diagenesis. They have also been successfully used to identify the source of TDS in formation waters and to distinguish between multiple sources of high TDS fluids.

Invited lecture

The effect of solubility decrease on geothermal power plant operation

Julia Scheiber

GEIE Exploitation Minière de la Chaleur, Kutzenhausen, France

e-mail: scheiber@soultz.net

Most geothermal resources provide 24/7 of heat and power production which makes geothermal one of the most stable base-load energy providers among the renewable energies. Profitability of geothermal power and heat plants depends on continuous operation of both geothermal loop and surface installations. Unscheduled shut-down times and intense maintenance operations due to scaling and corrosion related phenomena can decrease operation efficiency significantly and cause high follow-up costs and loss of revenues.

Geothermal fluids are characterized by their mineralization and by their natural gas load: Salinity can range from drinking water quality to several hundreds of grams of Total Dissolved Solids (TDS) and gas/liquid ratio can be very high. Chemical equilibrium of geothermal fluid is affected by pressure and temperature decrease and by contact with various materials of underground casing and surface installation.

Solubility decrease of dissolved minerals is usually simply triggered by temperature decrease or mixing of different brines which results in the formation of scales like amorphous silica, sulfate or sulfide minerals whereas calcium carbonate scale formation is usually triggered by pressure decrease and change of pH. Uncontrolled degassing of dissolved gases, partwise or fully, results in a two phase flow which is extremely corrosive at high flow velocities.

The Soultz-sous-Forêts geothermal site applies pressure control in the surface installation for calcium carbonate mitigation but faced in the past deposition of barium/strontium sulfate and metal sulfides due to the temperature decrease in the heat exchangers. Several issues are related to scale formation: Scaling in the heat exchangers increases friction and thereby pressure losses which affect negatively pressure control in surface installations downstream of the heat exchanger. Moreover, barium sulfate deposits act like an insulation layer and decrease efficiency of heat transfer. Frequent cleaning operations were required in the past to keep up efficiency but these operations are time and cost intensive. Cleaning operations are also an issue of safety at work due to the NORM (Naturally Occurring Radioactive Material) character of the scales which also results in high disposal costs.

Successful barium sulfate scale mitigation can be managed by continuous injection of phosphonic acid but metal sulfides are still formed. Currently an intense R&D study for metal sulfide mitigation is performed in cooperation with several other geothermal sites; first results will be presented in the lecture.

Invited lecture

Numerical simulations of CO_2 sequestration in basaltic rock formations: Challenges for optimizing mineral-fluid reactions

Alexander P. Gysi

Department of Geology and Geological Engineering, Colorado School of Mines, USA

e-mail: agysi@mines.edu

Carbonic acid is one of the major acids in natural waters and plays a fundamental role in geochemical cycles near the Earth's surface. Rapid anthropogenic CO_2 emissions have raised considerable concerns on their effects on climate change and several carbon capture storage options have been proposed. Mineral carbonation in mafic and ultramafic rocks is considered as a possible solution for permanently trapping CO_2 in geological rock formations. Optimizing the mineralization of CO_2 in basaltic rock formations requires a detailed knowledge of mineral-fluid reactions and their effects on chemical mass fluxes over different timescales. The alteration mineralogy associated with low temperature natural basaltic systems consists primarily of aluminum hydroxide and ferrihydrite, Mg–Fe smectites and Al–Si minerals (allophane and/or imogolite), whereas at higher reaction progress when more basalt has reacted, the mineralogy consists of Ca–Na zeolites, Fe–Mg-rich clay minerals and calcite [1]. Observations based on elevated CO_2–basalt alteration from the Disko-Nuussuaq Island (West Greenland) indicate a different mineral assemblage consisting of quartz, Fe–Mg and Ca–Mg carbonate solid solutions to be among the dominant secondary mineral assemblage [2]. Laboratory basaltic glass solubility experiments successfully reproduced this mineralogy at 75 ºC and pCO_2 of ~25 bar within 124 days, whereas at 40 ºC the mineralization included chemically similar but less crystalline phases [3,4]. These experiments showed that there are several ways of optimizing the amount of CO_2 mineralized including acid supply, temperature, fluid/rock ratios and reaction time.

We are still facing many challenges to better understand the long-term storage of CO_2 in geologic rock formations. Numerical simulations can be used to evaluate processes occurring at equilibrium vs. the ones driven by kinetics. Some of the major challenges that we will review include adequate mineral solid solutions models, mineral dissolution kinetics and available thermodynamic data for aqueous species and minerals (carbonates, smectites and zeolites). We will also explore the key factors affecting the interaction between CO_2-rich waters and basaltic rock formation using numerical simulations. The simulations will be compared to results from laboratory solubility experiments and to natural analogues where mineralization occurs on geological timescales. Numerical simulations were carried out using GEM-selektor (http://gems.web.psi.ch) for modeling aqueous solution – solid solutions interactions and reactive mass transport of CO_2-water-basalt interaction. The simulations indicate that the competing reactions between complex clay minerals (dioctahedral and trioctahedral Na-Ca-Mg-Fe smectites) and Fe-Mg-carbonates at low pH (~3-6), and zeolites and clay minerals (trioctahedral Na-Ca-Mg-Fe smectites) and calcite at high pH (~8-10), control the availability of Ca, Mg and Fe in aqueous solutions. A better understanding of these key mineral-fluid reactions and improvement of their thermodynamic activity models is critical for making predictive calculations. This comprises the basis for extending the simulations to reactive transport models and for the assessment of the feasibility of long-term carbonate mineralization in basaltic rock formations.

References

[1] P.S. Neuhoff, T. Fridriksson, S. Arnórsson. Porosity evolution and mineral paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, Eastern Iceland. *Am. J. Sci.* **299**, 467-501 (2006).
[2] K.L. Rogers, P.S. Neuhoff, A.K. Pedersen, D.K. Bird, CO_2 metasomatism in a basalt-hosted petroleum reservoir, Nuussuaq, West Greenland. *Lithos* **92**, 55-82 (2006).
[3] A.P. Gysi, A. Stefánsson, Mineralogical aspects of CO_2 sequestration during hydrothermal basalt alteration - An experimental study at 75 to 250 °C and elevated pCO_2. *Chem. Geol.* **306-307**, 146-159 (2012).
[4] A.P. Gysi, A. Stefánsson, CO_2-water-basalt interaction. Low temperature experiments and implications for CO_2 sequestration into basalts. *Geochim. Cosmochim. Acta* **81**, 129-152 (2012).

Invited lecture

Long-term behaviour of waste materials

Wolfgang Hummel

Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

e-mail: wolfgang.hummel@psi.ch

Solubility is considered as one of the “pillars of safety” in deep geological repository projects for radioactive waste. Most radionuclides produced by fission and neutron activation in nuclear reactors and in targets of particle accelerators are heavy metals, i.e. actinides, lanthanides, transition and post-transition metals. Many of them exhibit very low solubility in the ppm and even ppb range. These solubility limitations are an important geochemical effect in performance assessment studies concerning the long-term behaviour (in the range of thousands up to one million years) of planned repositories for radioactive waste.

Chemical thermodynamic data of the actinides Th, U, Np, Pu, Am and Cm, the transition metals Fe, Ni, Zr, Mo, Tc, the post-transition metal Sn, as well as Se and selected organic complexes with these elements have been reviewed within the scope of the OECD NEA TDB project (see OC 3). Many oral and poster communications in this conference present ongoing research and new data related to the chemical thermodynamics of safety relevant nuclides produced in nuclear power plants.

Recently, a further source of radioactive wastes came into focus of safety assessments related to geological repository projects: Long-lived radionuclides from research facilities like CERN and PSI, mainly produced in Pb and Pb/Bi targets of spallation sources. Some of these additional radionuclides are isotopes of Ti, Hg, Pb, Bi and Po. While Ti, Hg and Pb data have been reviewed in the past, Bi and Po data are largely unexplored.

In contrast to this detailed consideration of solubility and related equilibrium processes in radioactive waste repository projects, assessments of the long-term behaviour of landfills of non-radioactive wastes are close to non-existent.

Current legislation in Switzerland defines several types of landfills based on total concentrations of contaminants in the wastes and the results of 24-hours leach tests of waste forms. As a new feature, post-closure surveillance of landfills is foreseen for a maximum period of 50 years. This period can be shortened by the authorities to 15 or even 5 years, depending on the type of landfill, if “no harmful consequences to the environment are expected anymore”.

In radioactive waste repositories we have the effect of “natural attenuation” by radioactive decay of the contaminants. There is no such attenuation effect for toxic heavy metals in landfills. They will slowly be dissolved and washed out by intruding rain water and form a contaminant plume in the vicinity of the landfill.

By very simple estimation methods, I will show for a typical landfill containing municipal solid waste incinerator (MSWI) bottom ash that these wash out periods extend from hundreds to thousands of years. However, these results depend on an equally simple estimate of the time the pH buffer capacity of MSWI bottom ash may last. Hence, there is no guarantee that more sophisticated safety analyses, as routinely done for radioactive waste repository projects, would lead to the same results if applied to MSWI bottom ash landfills.

From the elements in the lists of total concentrations of contaminants in Swiss legislation, chemical thermodynamic data of the toxic heavy metals Cu, Pb, Cd, Zn, Hg have been scrutinised in a series of IUPAC reviews by members of SSED. Thermodynamic data for Ni and Sn have been reviewed in the mentioned OECD NEA TDB project. Data compilations for Sb data exist, whereas Cr, As, and Tl data are less explored. However, the main problem with the latter elements is not the lack of compilations but the lack of experimental data.

Keynote lecture

Solubility phenomena in Molten Salt Reactor fuel

Ondrej Beneš, Rudy J. M. Konings

European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany

e-mail: rudy.konings@ec.europa.eu

In recent years Molten Salt Reactors (MSR) have re-appeared in the focus of the nuclear reactor design due their appealing characteristics with respect to safety and resource utilisation. In this reactor type the fuel is a liquid salt containing the fissile and fertile material to maintain the nuclear chain reaction. The liquid salt also serves as the primary coolant, and as confinement of the fission products. In the traditional thermal spectrum MSR, the solvent for the fertile thorium and fissile uranium is the eutectic of LiF and BeF_2, whereas for the fast spectrum MSR a LiF-ThF_4 mixture is used as solvent for plutonium and/or uranium. Recently also attention for chloride-based fuel systems has emerged.

In this context we study phase diagrams and related thermodynamic properties of the relevant salts with experimental and computational techniques. Due to the specific chemical properties of the fluoride salts (corrosive, volatile, hygroscopic) high temperature experiments cannot be performed with standard techniques, which is further complicated when working with actinides, which are radioactive. In our work we have developed encapsulation techniques for calorimetric measurements that overcome these problems, in order to measure liquidus temperature, heat capacity and enthalpy of mixing. Thermodynamic models based on the CALPHAD technique are used to obtain a consistent multi-compound description of the relevant salts. In this lecture we will show how these techniques can be used to understand and predict solubility phenomena in liquid fluoride mixtures.

OC 15

Hydrolysis and solubility of Ni(II) under alkaline to hyperalkaline conditions and complex formation with ISA

Maria Rosa González-Siso[1], Xavier Gaona[2], Lara Duro[1], Marcus Altmaier[2], Jordi Bruno[1]

[1]Amphos 21, Passeig Garcia i Faria, 49-51, 1-1a, 08019 Barcelona, Spain
[2]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany

e-mail: maria.rosa.gonzalez.siso@gmail.com

The Swedish Final Repository (SFR1) is used for the final disposal of low- and intermediate-level radioactive waste (L/ILW) in Sweden. Cementitious materials are used in the SFR1 for the construction of galleries and vaults, but also as a component for the waste stabilization. These materials will impose highly alkaline pH conditions to the contacting groundwater. On the other hand, ^{59}Ni ($t_{1/2} = 7.5 \cdot 10^4$ a) and ^{63}Ni ($t_{1/2}$ = 96 a) are important contributors to the radiotoxicity of the wastes in SFR1. Moreover, under highly alkaline cement porewaters, cellulose is slowly degraded to one of the main representatives of polyhydroxy carboxylic acids: α-isosaccharinic acid (ISA). Hence, it is very important to understand and quantify the chemical interactions between Ni(II) and ISA in highly alkaline media. In this work we will present our most recent results concerning:

1. Solubility and hydrolysis of Ni(II) in the absence of ISA

The solution chemistry of Ni(II) is characterized by a moderate hydrolysis and the formation of the sparingly soluble $Ni(OH)_2(s)$ under alkaline to hyperalkaline pH conditions. The solubility of $Ni(OH)_2(s)$ has been investigated at $T = 22 \pm 2$°C under inert gas (Ar) atmosphere ($O_2 < 5$ ppm). Batch solubility experiments were performed from undersaturation conditions with a commercial $Ni(OH)_2(s)$. Independent batch samples were prepared using 20 mg $Ni(OH)_2(s)$ in 20 mL per experiment. Experiments were performed in 0.5 and 3.0 M NaCl–NaOH with $7.5 \leq pH_m \leq 13$ (with $pH_m = -\log m_{H^+}$). m_{Ni} and pH_m were monitored at regular time intervals for up to 310 days. Dissolved m_{Ni} was measured by ICP–MS after 10 kD ultrafiltration. The commercial $Ni(OH)_2(s)$ and the solid phase from selected solubility experiments in the absence and presence of NaISA after attaining equilibrium conditions were characterized by XRD. No solid phase alteration was observed. Our laboratory results indicate that there are not formation of Ni(II) anionic hydroxo species up to pH_m=13. A full thermodynamic model is presented for the solubility of $Ni(OH)_2(s)$ in dilute to concentrated NaCl solutions valid within the pH_m range 8 to 13.

2. Solubility of Ni(II) in the presence of ISA

Ni(II) solubility experiments in the presence of NaISA were conducted using the same solid phase (commercial $Ni(OH)_2(s)$) as the previous ones. NaISA(s) was synthesized from the alkaline degradation of commercial α-lactose hydrate. Independent batch samples were prepared in 0.5 M NaCl–NaOH–NaISA solutions with $0.01 \text{ M} \leq [ISA^-] \leq 0.2$ M and $9 \leq pH_m \leq 13$. m_{Ni} and pH_m were monitored at regular time intervals for up to 290 days.

Solubility data show a clear and gradually increase of Ni(II) solubility with increasing concentration of ISA. A larger increase in the solubility is observed for pH_m above ≈11. Our laboratory results are properly described with the definition of the aqueous species NiOHISA(aq) and $Ni(OH)_2ISA^-$. The increase in the solubility of Ni(II) predicted using the speciation scheme in the Thermochimie database [1] in the presence of ISA at $pH_m \geq 9.5$ (due to the formation of $Ni(OH)_3ISA^{2-}$) is not reproduced in the present work, although the formation of this species is also hinted in our solubility data at $pH_m \geq 12$. This observation is in line with the minor role of the species $Ni(OH)_3^-$confirmed in our solubility experiments in the absence of ISA up to pH_m = 13.

The work presented is a clear step forward in the quantification of the mobility of Ni(II) under the hyperalkaline conditions and in the presence of ISA expected in the SFR repository.

Reference

[1] www.thermochimie-tdb.com

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OC 16

Sulfur anions in alkaline solutions: some basic truths

Glenn Hefter, David Bátka, Maribel Navarro, Peter M. May

Chemistry Department, Murdoch University, Murdoch WA 6150, Australia

e-mail: g.hefter@murdoch.edu.au

The chemical reactivity of simple sulfur-containing anions such as sulfide (S^{2-}), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) is relatively well known in acid solutions. However, the behaviour of these species changes considerably when they are dissolved in strongly alkaline solutions. Understanding this behaviour is important because sulfur-containing minerals such as pyrite (FeS_2) and cinnabar (HgS) are commonly present in small amounts in the bauxite ores used to produce purified alumina via the well-known Bayer process. Such minerals dissolve in the hot concentrated NaOH(aq) used in the Bayer process producing a variety of sulfur anions which are thought to exert a strong influence on the redox chemistry of the Bayer solutions. This presentation details some surprising findings about the chemistry of sulfur-containing anions in strongly alkaline solutions obtained from detailed chemical analyses and Raman spectroscopy.

OC 17

The scope on structure rearrangements in solution by vibration spectroscopy methods. Calcium perchlorate – water system

Olga N. Pestova, Andrey Yu. Efimov, Lyubov A. Myund

Saint-Petersburg State University, Chemistry Institute, 198504, Saint-Petersburg, Universitetskiy av., 26. Russia.

e-mail: pestova-1980@mail.ru

Rearrangements of solution structure take place under the effect of salt concentration. Such structural irregularity is characteristic of salt-water systems in the post-eutectic concentration range if the salt can form several crystalline hydrates. Changes in the solution structure are reflected on the phase diagram of the system. Vibration spectroscopy methods give information about changes in parameters of the bands studied under the effect of salt concentration in solution. A correlation between spectral data and solubility polytherms is established by a chemometric analysis.

NIR, Raman and ATR FTIR spectra have been measured of aqueous calcium perchlorate solutions in the wide concentration range at 25°C. By the methods of Principal Component Analysis (PCA) and Multivariate Curve Resolution - Alternating Least Squares (MCR-ALS) the number, spectra and concentration profiles have been determined of spectral forms of water and ClO_4^- ion in solutions. The results have been analyzed using a phenomenological model. Concentration ranges for structural rearrangements of the solution, the nature of structural micro-irregularities and different states of ClO_4^- -ion are established.

OC 18

Solubility of radium sulfate and carbonate in sodium chloride media

Artem V. Matyskin[1], Paul L. Brown[2], Christian Ekberg[1]

[1]Nuclear Chemistry and Industrial Material Recycling, Department of Chemistry and Chemical Engineering,
Chalmers University of Technology, Kemivägen 4, SE-412 96 Göteborg, Sweden
[2]Rio Tinto Technology and Innovation, 1 Research Avenue, Bundoora VIC 3083, Australia

e-mail: matyskin@chalmers.se

Radium is a Naturally Occurring Radioactive Material (NORM) and can be found in the environment. Due to the long half-life of 1600 years and the relatively high abundance of the parent nuclide (^{238}U) ^{226}Ra is the most abundant radium isotope. Its migration from man-made wastes is of major concern in environmental science. Modelling of the migration process requires reliable experimental data of solubilities. Such data are limited for radium compounds because of the fact that radium has no stable isotopes and is extremely toxic.

In this work 7 mL of 0.40 ± 0.02 mM radium solution was prepared and used to investigate the solubility of $RaSO_4$ and $RaCO_3$ from oversaturation using sodium sulfate and sodium carbonate. Sodium chloride was used as a background electrolyte to maintain constant ionic strength. Solubility was determined over a wide range of NaCl concentrations (0.3 – 5.5 M for $RaSO_4$ and 1.3 – 5 M for $RaCO_3$) in a CO_2 atmosphere and at 25.1 °C. Samples were centrifuged for 1 hour at 50000 G to separate the solid and aqueous phases. Radium concentration was measured using a High Purity Germanium Detector. The extended specific ion interaction theory was adopted to include $RaSO_4$(aq) and $RaCO_3$(aq) ion pair formation and complexation of $NaSO_4^-$(aq) and $NaCO_3^-$(aq).

Solubility product constants were extrapolated to zero ionic strength ($\log_{10} K_{sp}^\circ = -10.16 \pm 0.05$ for $RaSO_4$ and $\log_{10} K_{sp}^\circ = -7.73 \pm 0.56$ for $RaCO_3$). It was found that the solubility curves of $RaSO_4$ and $RaCO_3$ have a similar shape as those of $BaSO_4$ and $BaCO_3$, respectively. It can be supposed that Ra^{2+} and Ba^{2+} undergo similar specific ion interactions in NaCl media, probably due to the fact they have the same charge and similar effective ionic radii.

OC 19

Formation, stability and solubility of ternary Nd(III)–OH–Cl(s) phases in dilute to concentrated Na–Mg–Ca–Cl solutions

Michel Herm, Xavier Gaona, David Fellhauer, Volker Metz, Marcus Altmaier, Horst Geckeis

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany

e-mail: michel.herm@kit.edu

In safety analyses for deep geological nuclear waste repositories a reliable prediction of the chemical behavior of actinides in aqueous solutions is necessary. Although geological or geo-technical barrier systems may retard or prevent formation water from contacting the waste, intrusion of aqueous solutions into a repository has to be taken into account within the long-term evolution of these facilities. Porewater in certain sedimentary bedrocks as well as water potentially intruding salt rock repositories will be characterized by elevated ionic strength and high Na^+, Mg^{2+}, K^+ and Cl^- concentrations. Trivalent (An^{III}) and tetravalent (An^{IV}) actinides are assumed to prevail under the reducing conditions expected after the closure of a deep geological repository for nuclear waste.

An appropriate knowledge of the solubility controlling solid phases is mandatory in source term estimations and for reliable geochemical calculations. $An^{III}/Ln^{III}(OH)_3(s)$ phases are usually considered as solubility limiting solid phases of trivalent actinides/lanthanides in dilute to concentrated saline systems in the absence of complexing ligands. The successful synthesis of ternary An^{III}/Ln^{III}–OH–Cl(s) phases has been reported in structural studies, but no thermodynamic data has been derived so far for these systems [1, 2]. In this study Nd(III) is used as chemical analog for trivalent actinides.

In a first part of this work, the transformation of $Nd(OH)_3(s)$ into a ternary Nd–OH–Cl solid phase was experimentally assessed in NaCl (5.61 m), $MgCl_2$ (0.25–5.15 m) and $CaCl_2$ (3.91 m) systems as a function of pH ($7.5 \leq pH_m \leq 9.6$) and temperature ($T = 22$ and 80°C). Solid phase characterization shows a clear transformation of the initial solid phase into $Nd(OH)_2Cl(s)$ in ≥ 3.87 m $MgCl_2$ systems at $T = 22$ and 80°C.

In a second part of the present study, batch solubility experiments were performed under argon atmosphere at room temperature using the $Nd(OH)_2Cl(s)$ phase synthesized at $T = 22$°C. Experiments were performed from undersaturation in 5.61 m NaCl, 2.11–5.15 m $MgCl_2$, 2.68/3.91 m $CaCl_2$ and $7.0 \leq pH_m \leq 13$.

The comparison of $Nd(OH)_2Cl(s)$ and $Nd(OH)_3(s)$ solubility determined under analogous experimental conditions [this work, 3] shows significantly lower m_{Nd} (up to 1.5 lg-units) in equilibrium with $Nd(OH)_2Cl(s)$ in 2.11–5.15 m $MgCl_2$ and 2.68/3.91 m $CaCl_2$ at $pH_m \leq 8.8$. On the contrary, no differences in aqueous concentrations in experiments with $Nd(OH)_2Cl(s)$ and with $Nd(OH)_3(s)$ are observed in 5.61 m NaCl within $7.5 \leq pH_m \leq 13$. The combination of the experimental solubility data determined in this work in $MgCl_2$ and $CaCl_2$ solutions with the Pitzer activity model derived in [3] allows the quantification of $\lg {}^*K^\circ_{s,0}\{Nd(OH)_2Cl(s)\} = 10.56 \pm 0.10$. The formation of the newly characterized solid phase is expected to have relevant implications in the source term of trivalent actinides for repository concepts where elevated chloride concentrations are expected.

References

[1] R.A. Zehnder, D.L. Clark, B.L. Scott, R.J. Donohoe, P.D. Palmer, W.H. Runde, D.E. Hobart, *Inorg. Chem.* **49**, 4781-4790 (2010).
[2] V.I. Bukin, *Dokl. Akad. Nauk SSSR* **207**, 1332-1335 (1972).
[3] V. Neck, M. Altmaier, Th. Rabung, J. Lützenkirchen, Th. Fanghänel, *Pure Appl. Chem.* **81**, 1555-1568 (2009).

OC 20

Oxygen solubility modelling in water and brines

Frank Bok[1], Helge C. Moog[2]

[1]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology
[2]Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) gGmbH

e-mail: f.bok@hzdr.de

Dissolved molecular oxygen influences the chemistry of various redox reactions in the aqueous solution *e.g.* corrosion processes, microbial activity or the immobilisation of radionuclides. In the presence of dissolved oxygen, the poorly soluble (hydro)oxides of reduced actinides, *e.g.* $U(OH)_4$(am), PuO_2(am/cr) get oxidized and these elements become more soluble in water. Furthermore, the activity of dissolved oxygen is used as redox parameter in common geochemical codes (*i.e.* Geochemist's Workbench®). Thus, the correct prediction of the O_2 solubility in water and saline solutions is necessary for the correct modelling of redox processes in water and in brines especially.

For reasons of consistency, the few existing sets of O_2-ion interaction coefficients for the Pitzer model cannot be used in combination with the THEREDA Pitzer model for the oceanic salt system and would result in wrong gas solubility calculation's results. Therefore, a new and consistent set of solubility parameters was deduced using published O_2 solubility data in water and binary and ternary salt solutions from ~100 literature references.

First a critical review of the published data on oxygen solubility in water and salt solutions has been performed. Using these data, the temperature function of the O_2 Henry's constant could be obtained valid for the temperature range 273–618 K. Then a consistent set of Pitzer interaction coefficients including its temperature function's parameters was deduced for the calculation of the amount of dissolved oxygen in aqueous solution and brines. All parameters have been determined using the geochemical speciation software PHREEQC coupled with the parameter estimation software UCODE-2005.

A self-consistent set of Pitzer interaction coefficients for the description of oxygen solubility in binary and some ternary salt solutions could be obtained for the system Na^+, K^+, H^+, Ca^{2+}, Mg^{2+} / Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, OH^- - $H_2O(l)$. For the chloride and the sulphate subsystems, temperature function parameters could be obtained to describe the temperature dependency of the O_2 solubility in these salt solutions.

OC 21

New comprehensive thermodynamic model for the solubility of $TcO_2{\cdot}xH_2O$(am) in the aqueous Tc^{4+}–Na^+–Mg^{2+}–Ca^{2+}–H^+–Cl^-–OH^- system

Ezgi Yalcintas, Alexander Baumann, Xavier Gaona, Marcus Altmaier, Horst Geckeis

Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany

e-mail: ezgi.yalcintas@kit.edu

Technetium–99 is a β–emitting radionuclide produced in nuclear reactors by the fission of ^{235}U and ^{239}Pu. Due to its significant inventory in spent nuclear fuel, long half-life ($t_{½}$ ~211.000 a) and redox-sensitive character, ^{99}Tc is a very relevant radionuclide in Performance Assessment exercises of repositories for radioactive waste disposal. Under sub-oxic/oxidizing conditions, technetium exists as the highly soluble and mobile pertechnetate anion (TcO_4^-). In reducing environments Tc(IV) prevails, forming sparingly soluble hydrous oxides ($TcO_2{\cdot}xH_2O$(s)). The later redox state is expected to dominate the aqueous chemistry of Tc under the reducing conditions predicted for deep geological repositories. In this framework, an appropriate understanding of the solubility and hydrolysis of Tc(IV) in dilute to concentrated saline systems is required for an accurate assessment of technetium source term in repositories for radioactive waste disposal.

The solubility of Tc(IV) was investigated in a comprehensive experimental approach from undersaturation conditions in 0.1–5.61 m NaCl, 0.1–4.58 m KCl, 0.25–5.15 m $MgCl_2$ and 0.25–5.25 m $CaCl_2$ solutions in the pH_m range 1.5–14.6. Experiments were performed at 22 ± 2°C in Ar gloveboxes with < 2 ppm O_2. Strongly reducing conditions (pH + pe < 4) were fixed in each independent solubility sample with $Na_2S_2O_4$, $SnCl_2$ or Fe powder. Technetium concentration, pH_m and E_h values were monitored at regular time intervals over several months. Thermodynamic equilibrium was assumed after repeated measurements with constant [Tc] and pH_m. After attaining equilibrium conditions, the redox speciation of technetium in the aqueous phase was quantified for selected samples using solvent extraction with TPPC and XANES analysis. Solid phases of selected batch experiments were further characterized by XRD, SEM–EDS and quantitative chemical analysis. Additional solubility experiments were conducted in "simulated systems", based on reported ground water and cementitious pore water compositions with complex mixtures of NaCl–KCl–$MgCl_2$–$CaCl_2$.

Solid phase characterisation and solubility data indicate that $TcO_2{\cdot}0.6H_2O$(s) is the solid phase controlling the solubility of Tc(IV) in all the evaluated systems. The combination of solvent extraction and XANES analysis confirms the predominance of Tc(IV) in the aqueous phase, independently of the salt system and concentration. The solubility of $TcO_2{\cdot}0.6H_2O$(s) decreases with a well-defined slope (log [Tc] vs. -log [H^+]) of –2 in acidic dilute systems. The same slope is retained in concentrated brines, although a very significant increase in the solubility (up to 4 orders of magnitude) is observed with increasing ionic strength. A newly derived chemical model based on these solubility data in combination with spectroscopic evidences reported in the literature, best explains this increase considering the formation of the previously unreported trimeric technetium species $Tc_3O_5^{2+}$. In the near-neutral pH region, the pH-independent behaviour of the solubility is consistent with the chemical reaction $TcO_2{\cdot}0.6H_2O(s) + 0.4\ H_2O \rightleftharpoons TcO(OH)_2(aq)$ with a $\log_{10}{}^{*}K^{\circ}_{s,TcO(OH)2}$ in good agreement with the current NEA–TDB data selection. The amphoteric behaviour of Tc(IV) is confirmed by the formation of the species $TcO(OH)_3^-$ in dilute NaCl and KCl systems with $pH_m \geq 11$. The same speciation is retained in concentrated alkaline NaCl and KCl solutions, although a decrease in solubility compared to dilute systems takes place due to ion interaction processes. Changes in the aqueous speciation are observed in concentrated alkaline $MgCl_2$ and $CaCl_2$ brines, where the formation of $Mg_3[TcO(OH)_5]^{3+}$ and $Ca_3[TcO(OH)_5]^{3+}$ ternary species are proposed based on the slope analysis of the corresponding solubility curves and the comparison with previous observations available for An(IV) and Zr(IV) in concentrated $CaCl_2$ solutions. The formation of these species has been recently validated by quantum chemical calculations performed at KIT–INE. Based on the newly generated experimental data, comprehensive chemical, thermodynamic and activity models using both SIT and Pitzer approaches are derived for the system Tc^{4+}–Na^+–K^+–Mg^{2+}–Ca^{2+}–H^+–Cl^-–OH^-–H_2O at 25°C. These data complement and significantly extend the current thermodynamic selection of the OECD Nuclear Energy Agency (NEA–TDB). Tc(IV) solubility investigated in "simulated real systems" is in good agreement with qualitative predictions based on pure systems.

OC 22

Experimental determination of solubilities of brucite [$Mg(OH)_2(cr)$] in Na_2SO_4 solutions with Bborate to high ionic strengths: Formation constant for $MgSO_4(aq)$ and Pitzer interaction parameters for $MgB(OH)_4^+$—SO_4^{2-} [A]

Yongliang Xiong

Sandia National Laboratories (SNL)[B], Carlsbad Programs Group, 4100 National Parks Highway, Carlsbad, NM 88220, USA

e-mail: yxiong@sandia.gov

Sulfate is a major species in some natural brines associated with salt formations. For instance, the sulfate concentrations in the Waste Isolation Pilot Plant (WIPP) brines are 0.203 $mol·kg^{-1}$ and 0.187 $mol·kg^{-1}$ in the Generic Weep Brine (GWB) and U.S. Energy Research and Development Administration Well 6 (ERDA-6), respectively, and 0.18 $mol·kg^{-1}$ in the Q brine at the Asse repository in Germany. Industrial-grade MgO consisting mainly of the mineral periclase is the only engineered barrier certified by the Environmental Protection Agency (EPA) for emplacement in the WIPP, a U.S. DOE geological repository for defense-related transuranic (TRU) waste in the bedded salt formation in New Mexico, USA. Notice that brucite is the hydrated phase of the engineered barrier, MgO, for the WIPP. An $Mg(OH)_2$-based engineered barrier consisting mainly of the mineral brucite is to be employed in the Asse repository in Germany. In addition, the borate concentrations in the WIPP brines GWB and ERDA-6, are 0.178 $mol·kg^{-1}$ (or 0.0445 $mol·kg^{-1}$ if it is expressed as $B_4O_7^{2-}$) and 0.0704 $mol·kg^{-1}$ (or 0.0176 $mol·kg^{-1}$ if it is expressed as $B_4O_7^{2-}$), respectively. Therefore, accurate knowledge about the solubility of brucite in sulfate solutions is important to the performance of the engineered barrier.

In this work, a solubility study on brucite in Na_2SO_4 solutions, up to 1.8 $mol·kg^{-1}$, with borate, has been conducted at 25°C. Based on the solubility data, the formation constant for $MgSO_4(aq)$ and the Pitzer interaction parameters for $MgB(OH)_4^+$—SO_4^{2-} are evaluated using the Pitzer model. The formation constant for $MgSO_4(aq)$ at 25°C and infinite dilution obtained in this study is in excellent agreement with the literature values.

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Keynote lecture

Computer assisted modelling (*ab initio*, molecular dynamics and Monte Carlo)

Sergey Churakov

University of Bern, Institute of Geological Sciences, Baltzerstrasse 1+3, CH-3012 Bern, Switzerland
Paul Scherrer Institut, Laboratory for Waste Management, CH-5232 Villigen PSI, Switzerland

e-mail: sergey.churakov@psi.ch

Atomistic modeling is a powerful tool which is widely used to elucidate structure of solids and aqueous solutions, as well as to predict their thermodynamics properties at conditions not easily accessible by experimental studies. Growing computational power and advances in numerical algorithm make molecular modeling an ever-growing field. However, as any theoretical method, molecular simulations have certain range of applicability. Each particular modelling approach relies on a set of assumptions, which limits the range of accessible systems or conditions. All these assumptions and limitations need to be carefully considered. I will start with a short overview of the atomistic modelling approaches (molecular dynamics, Monte Carlo) and emphasize the underlying assumptions and simplifications used in these methods (*ab initio* approaches, empirical force fields). Then, I will discuss some advanced simulation techniques which helps to overcome limitation related to short simulations times and the size of the modelled systems. Finally, I will present some applications of different simulation techniques to tackle thermodynamic aspects of fluids and fluid-mineral interfaces at different scales and levels of complexity.

OC 23

In Silico rational solvent selection: COSMO-RS prediction of solubility, cocrystallization, and solvate formation

Frank Eckert[1], Christoph Loschen[1], Andreas Klamt[1,2]

[1] COSMO*logic* GmbH & Co. KG, Burscheider Str. 515, 51381 Leverkusen, Germany
[2]Institute of Physical and Theoretical Chemistry, University of Regensburg, Regensburg, Germany

e-mail: eckert@cosmologic.de

It is demonstrated that the quantum chemistry based fluid phase thermodynamics theory COSMO-RS [1] is able to provide thermodynamic property information central to the task of rational solvent screening in the formulation process of pharmaceuticals (APIs). COSMO-RS based workflows for the screening of solubility [2], cocrystal [3], and solvate formation [4] tendencies are presented. It is shown that the excess enthalpy of API-coformer mixture is an excellent descriptor for the tendency of two compounds to co-crystallize, opening up a pathway to identify potential new co-crystals with decent effort on large sets of molecules. A closely related approach is applied to the identification of drug-solvent pairs that most likely form crystalline solvates. Due to the fact that many solvates form inclusion compound, the solvent shape is another important factor influencing solvate formation. Using an extensive dataset a simple and statistically robust model is developed which allows for the assessment of a solvent's ability to form a solvate. The approach ranks a solvate before any non-solvate by a probability of about 80% and thus can help to identify suitable solvents early in the drug development process and thus save precious resources. Last but not least, the presentation aims to raise awareness of the omnipresence of the solvate phenomenon, and addresses its implications for experimental data sources and model building.

Keywords: solubility; cocrystals; solvates; in silico modeling; COSMO-RS;

References

[1] A. Klamt, *J. Phys. Chem.* **99**, 2224 (1995); F. Eckert, A. Klamt, *AIChE J.* **48**, 369 (2002); A. Klamt, F. Eckert, W. Arlt, *Ann. Rev. Chem. Biomol. Eng.* **1**, 101 (2010).
[2] A. Klamt, F. Eckert, M. Hornig, M.E. Beck, T. Bürger, *J. Comp. Chem.* **23**, 275 (2002).
[3] Y.A. Abramov, C. Loschen, A. Klamt, *J. Pharm. Sci.* **101**, 3687 (2012).
[4] C. Loschen, A. Klamt, *in preparation*.

Keynote lecture

An overview of novel computational methods for equilibrium and kinetic calculations

Allan Leal

Institute of Geophysics, ETH Zürich, Switzerland

e-mail: allan.leal@erdw.ethz.ch

Efficient and robust computational methods for chemical equilibrium and kinetic calculations are becoming increasingly needed for intensive simulations of coupled physical and chemical processes. These include both industrial and natural applications, such as waste nuclear disposal, geologic carbon storage, geothermal energy systems, enhanced oil recovery, soil and groundwater remediation, and so forth. The physical processes in such applications are usually of conservative nature, mathematically described by partial differential equations that model conservation of mass, momentum, and energy. The chemical processes are usually coupled to the physical processes via reaction source terms, governed by kinetic laws, that describe the rates of production or consumption of chemical species in the transport equations (e.g., advection-diffusion-reaction equations). In some particular applications, such as reactive fluid flow in porous media, where some geochemical reactions can have rates considerably faster than transport and fluid flow rates (e.g., reactions involving aqueous species only), it is reasonable to assume these reactions to be continuously in equilibrium. This has the effect of instantaneously bringing the reaction state to equilibrium whenever it is disequilibrated. Thus, from this partial local equilibrium assumption emerges the need for efficient chemical equilibrium calculations in addition to chemical kinetic calculations.

These two classes of chemical calculations are performed at every node of a mesh discretizing the medium where the coupled processes are simulated. For transient reactive fluid flow simulations, therefore, hundreds to millions of equilibrium and kinetic calculations are needed at every time step. Thus, it becomes apparent why we need specialized chemical methods for such intensive applications, where equilibrium and kinetic calculations should not only be solved as quickly as possible, but should also be resilient to unfeasible inputs that originate from non-physical, numerical perturbations introduced by the solution of the partial differential equations. In this talk, I present an overview of novel methods for multiphase equilibrium calculations based on both the Gibbs energy minimization (GEM) approach and on the solution of the law of mass-action (LMA) equations. I also describe a new approach towards the solution of the mixed kinetic-equilibrium problem, where some species are controlled by chemical equilibrium, while others by kinetic rates of reactions. Examples of their usage are given in the context of geochemical modeling and reactive transport simulations in porous media. The equilibrium and kinetic methods should, however, be effective for any type of chemical systems other than those involving aqueous, gaseous, and mineral species, since they are formulated without any specific chemical detail that could compromise its generality.

OC 24

Use of kinetically constrained free energy models for concentrated aqueous systems at 25-100 °C

Risto Pajarre, Pertti Koukkari, Petteri Kangas

VTT – Technical Research Centre of Finland, FI02044-VTT

e-mail: risto.pajarre@vtt.fi

The typical temperature range of aqueous processes encountered in process industries is from ambient to ca. 100 C. Within this temperature range, the Pitzer interaction parameters often provide useful approximations even for practical process evaluation, provided that the multicomponent models, typically applying Gibbs free energy minimisation for solubility equilibria, have been assessed for the said temperature range. However, most of the available databases tend to confine to data in ambient conditions. A database has been collected for modelling aqueous electrolyte solutions between temperatures 25-100 C. The main components are the ionic species Na(+)/K(+)/H(+)/Ca(+2)/Mg(+2) and Cl(-)/OH(-)/CO_3(-2)/SO_4(-2) with additional metallic components used for mine and metallurgical calculations. Model has been applied to ash leaching and hydrometallurgical and mine water calculations.

As the practical system quite often will not reach equilibrium or must be controlled by time dependent reaction kinetics, the Constrained Free Energy method (CFE) can be applied. In such case, reaction extent constrained partial equilibrium can be calculated as a series of intermediate states before reaching the global equilibrium. For such intermediate states with fast partial equilibria between solute species, pH as a measurable intensive quantity can be used as the key modelling parameter. The novel method is illustrated with an example of precipitated calcium carbonate (PCC) process. PCC is formed by simultaneous injection of CO_2 and $Ca(OH)_2$ slurry in to the reactor. Measured pH from the reactor could be used to assess reaction kinetic parameters in a model that used the reaction affinities to illustrate the tendency for the system, via an aqueous quasi stationary state, to develop towards a stage of slow $CaCO_3$ precipitation. To remove the retarded reaction, a chemical additive could be used to obtain desired shift towards zero affinity state at the end of reaction zone.

The presentation will cover examples of the advanced database as well as featuring of the kinetically constrained solution models and their usage within Gibbs energy minimisation algorithms.

OC 25

Thermodynamic modeling of the solubility of silica

Kaj Thomsen

Center for Energy Resources Engineering, DTU Chemical Engineering, Technical University of Denmark, 2800 Lyngby, Denmark

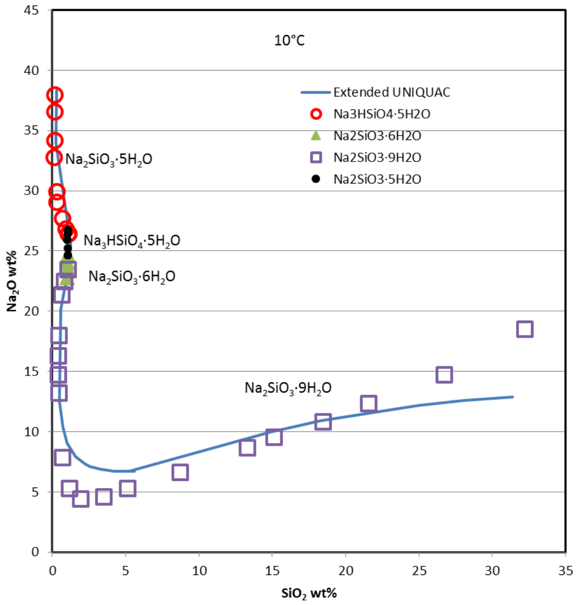
e-mail: kth@kt.dtu.dk

Silica scaling is the deposition of solid silica compounds in for example hot water heat exchangers. Silica is also an ingredient in industrial products such as water glass and cement. Another possible use of silicate minerals is for carbon dioxide storage.

In this project, it is attempted to model the solubility of silica in water under industrial conditions, including pressures up to a few hundred bar. A thermodynamic model for silica solubility is useful for simulating industrial processes using silica. It can help to avoid problems caused by silica scaling and help to determine how to re-dissolve silica deposits.

The thermodynamic model used is the Extended UNIQUAC model that combines the extended Debye-Hückel equation with the local composition activity coefficient model UNIQUAC.

It was found that many systems can be modeled by considering three aqueous silica species: SiO_2, SiO_3^{2-}, and $HSiO_3^-$. The solubility of silica in aqueous solutions of alkali metal oxides and carbonates is quite high. A phase diagram at 10°C for the SiO_2 – Na_2O – H_2O system is shown in figure 1.



The four solid phases formed in the system at this temperature are:

1. $Na_3HSiO_4 \cdot 5H_2O = 3NaOH \cdot SiO_2 \cdot 4H_2O$
2. $Na_2SiO_3 \cdot 5H_2O$
3. $Na_2SiO_3 \cdot 6H_2O$
4. $Na_2SiO_3 \cdot 9H_2O$

These four solids are all described as consisting of Na^+, SiO_2, SiO_3^-, and H_2O.

Fig. 1: Phase diagram for the SiO_2 – Na_2O – H_2O system at 10 °C

OC 26

Advanced analysis of isobaric heat capacities by mathematical gnostics

Zdeněk Wagner

E. Hála Laboratory of Separation Processes, Institute of Chemical Process Fundamentals of the CAS,
v. v. i. Rozvojová 2/135, CZ-16502 Prague 6, Czech Republic

e-mail: wagner@icpf.cas.cz

In this work the applicability of mathematical gnostic to small samples of highly scattered heat capacity experimental data is demonstrated. It is shown that these data do not have normal distribution and it is explained how such data can be analyzed. Application of the algorithms of mathematical gnostics allowed us to detect an abnormality in the measured data. This finding was analyzed using the laws of thermodynamics and compared with information available in the literature. This allowed us to formulate recommendation for performing heat capacity measurements.

OC 27

Enthalpy – entropy compensation in solvation

W. Earle Waghorne

School of Chemistry, University College Dublin, Ireland

e-mail: earle.waghorne@ucd.ei

Ben Naim, in a series of solvent papers published in the late 1970s [1], presented a theorem which states that, at infinite dilution, the solute induced structural changes in the solvent do not contribute to the free energy changes for processes occurring in solution, although they do contribute to the enthalpy and entropy changes. In effect, this states that the enthalpic and entropic contributions arising from modification of solvent structure around the solute exactly compensate, so that the free energy of solvation, for example, depends solely on the solute–solvent interactions.

This result has been widely neglected, despite its obvious importance to the understanding of solvation and processes involving solvated species. In part, this reflects the difficulty in separating the effects of the direct solute–solvent interactions from those effects that arise from the modification of solvent–solvent interactions by the solute.

Application of simple solvation models [2] to the thermodynamic transfer parameters of electrolytes between solvents and, in particular, to mixed solvents provides the possibility of separating these effects.

Figures 1 and 2 below illustrate two extremes. In aqueous methanol solvents the marked curvatures in the plots of $\Delta_{tr}H$ and $-T\Delta_{tr}S$ result from changes in solvent–solvent interactions and the linear variation in $\Delta_{tr}G$ reflects random solvation, while in mixtures of propylene carbonate and DMSO the thermodynamic transfer parameters are almost entirely the effect of preferential solvation (of Ag^+ by DMSO).

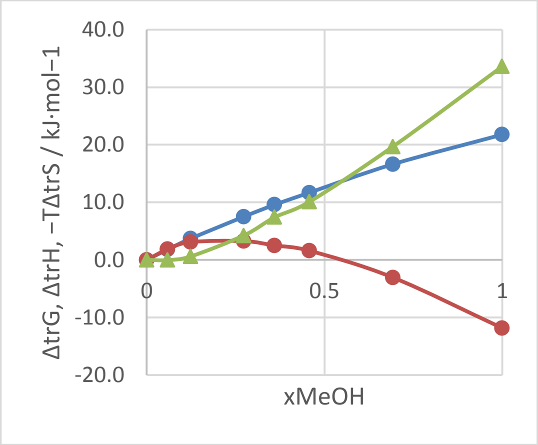


Fig. 1: Free energies (circles), enthalpies (diamonds) and entropies (as $-T\Delta_{tr}S$, triangles) of NaCl from water to aqueous methanol mixtures against methanol mole fraction

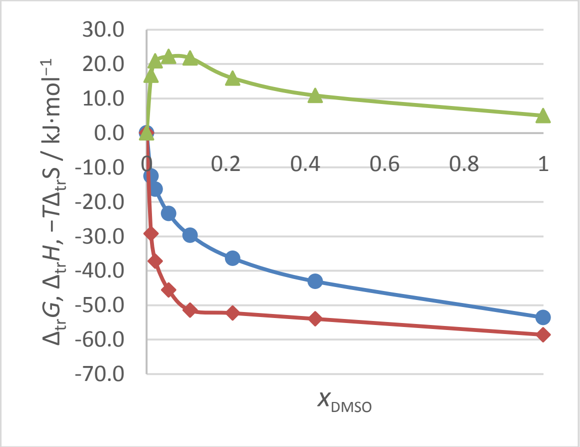


Fig. 2: Free energies (circles), enthalpies (diamonds) and entropies (as $-T\Delta_{tr}S$, triangles) of AgCl from propylene carbonate to propylene carbonate – DMSO mixtures against DMSO mole fraction

References

[1] A. Ben-Naim, A simple model for demonstrating the relation between solubility, hydrophobic interaction, and structural changes in the solvent. *J. Phys. Chem.* **82**, 874-885 (1978) and references therein.

[2] W.E. Waghorne, Thermodynamics of solvation in mixed solvents. *Chem. Soc. Rev.* **22**, 285-292 (1993).

OC 28

Kinetics of aqueous glass dissolution: effect of magnesium, secondary minerals and surface area

Bruno M.J. Thien

Paul Scherrer Institut (Laboratory for Waste Management) and ETH Zürich (Earth Sciences Department)

e-mail: bruno.thien@psi.ch

Dissolution kinetics of glass is investigated because glass is used as a matrix for waste radionuclide storage, and also because basaltic glass constitutes an essential part of the protolith in basaltic formations like Icelandic hydrothermal systems.

Glass is a metastable material, but the formation of a protective gel layer limits its alteration. It is commonly admitted that the precipitation of secondary minerals enhances the glass dissolution, by partially dissolving the gel. The presence of Mg in the system facilitates the precipitation of secondary minerals and therefore the dissolution of the glass. On the other hand, it had been found that Mg can also be incorporated within the gel as a charge compensator, increasing its protective properties. The distribution of Mg between the gel and the secondary phases depends on the pH of the solution.

In addition, field observations and geochemical modeling evidence the importance of glass specific surface area on its dissolution kinetics.

Keynote lecture

Thermodynamics of oxide systems as a function of particle size and surface chemistry

Juraj Majzlan

Institute of Geosciences, Burgweg 11, D-07749 Jena, Friedrich-Schiller University, Germany

e-mail: juraj.majzlan@uni-jena.de

A number of oxides are important for natural systems, remediation, and technology; one of the best examples are the iron oxides. The system Fe_2O_3-H_2O is represented by a variery of phases: goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akaganeite (β-FeOOH), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3), ferrihydrite ($\sim Fe(OH)_3$), and many others. Our thermodynamic measurements show that the stable coarse-grained (bulk) phases in this system are only hematite and goethite (depending on water activity); the other minerals are metastable. Despite their metastability, all phases mentioned above are present in the environment not only as single phases but also as mixtures. Their persistence may not only be due to kinetic factors and small differences in Gibbs energy, but also to free energy variations with the particle size. If very fine particles are formed, the energy stored in their surfaces and interfaces becomes a significant contribution to the overall enthalpy and Gibbs free energy of the phase.

Surface enthalpy of different iron oxides varies from 0.34 J/m^2 to 1.2 J/m^2. The enthalpies of water adsorption are crucial for the interpretation of the surface enthalpy measurements. Our data suggest that a) the least stable phase (i.e., the phase with the highest enthalpy with respect to the stable assemblage) has the lowest surface enthalpy and that 2) the anhydrous phases (e.g., hematite) have higher surface enthalpies than the hydrated phases (e.g., goethite). The competition between surface energy and polymorphism in the Fe-O(H) system creates energy cross-overs, which will be discussed as a function of the particle size, hydration level of their surfaces, and temperature. These energy cross-overs explain the co-existence of several iron oxide phases and the complexity of their occurrence in the environment.

For the least stable phase, ferrihydrite, we also explored the effect of surface loading or formation of ternary complexes. The enthalpies of solution of these samples in 5 *N* HCl were then measured by acid-solution calorimetry. The dissolution enthalpies are markedly different for the pure ferrihydrite and for the HFO samples with adsorbed anions. The dissolution enthalpies (ΔH_{diss}) of pure ferrihydrite vary between -510 and -570 J/g (depending on the crystallinity of ferrihydrite). On the other hand, the ΔH_{diss} for HFO with adsorbed arsenate, phosphate, or sulfate are significantly less exothermic, indicating stabilization of the iron oxide nanoparticles by the adsorption of the anions. The $\Delta\square H_{diss}$ values for the HFO with adsorbed anions vary between -370 and -270 J/g. Currently, we are calculating the formation enthalpies of the HFO with adsorbed anions in order to assess its stability with respect to the crystalline iron oxides and the crystalline iron oxysalts (sulfates, arsenates, phosphates).

Other systems, such as aluminium oxides or spinels, were also investigated in a detail by similar techniques, and will be discussed in this presentation. The observations made on iron oxides can be generalized to these, and perhaps to all, systems.

OC 29

Melting temperatures and solubilities of $Zn(NO_3)_2 \cdot 4H_2O$ nanocrystals confined in mesoporous materials

Tobias Grünzel, Michael Steiger

Department of Chemistry, University of Hamburg, Germany

e-mail: tobias.gruenzel@chemie.uni-hamburg.de

The Gibbs energy of nanocrystals increases with decreasing crystal size due to an increasing surface to volume ratio (A/V) resulting in a solubility increase and a melting temperature decrease of small crystals. The additional energy of a small crystal is accounted for by the surface energy γ yielding an expression for the solubility increase of nanocrystals. For the thermodynamic solubility product of small crystals we obtain [1]:

$$\ln K = \ln K_\infty + (\gamma_{\mathrm{cl}} V_{\mathrm{m}}/\mathrm{RT})\,(\mathrm{d}A/\mathrm{d}V) \qquad (1)$$

where K and K_∞ are the thermodynamic solubility product of the small and an infinitely large crystal, respectively, γ_{cl} is the surface free energy of the crystal–liquid interface, V_{m} is the molar volume of the solid, R is the gas constant and T is the absolute temperature. The surface to volume ratio is inversely proportional to the crystal size. For a spherical crystal of radius r, $\mathrm{d}A/\mathrm{d}V = 2/r$. The solubility curve of a hydrated salt, i.e. the relation between composition of the saturated solution and temperature, is a continuous function with a maximum if temperature is the ordinate and composition the abscissa. The maximum of the curve is the melting temperature of the hydrated solid and the composition of the saturated solution (the solubility at the melting temperature) equals the composition of the solid. Therefore, as shown in Fig.1, the melting temperature decrease ΔT_{m} of a small crystal corresponds to a solubility increase Δm_{sat}. Thus, the solubility increase of small crystals can be determined indirectly by measurement of the melting temperature. In the present study, we have determined the melting temperatures of nanocrystals of zinc nitrate tetrahydrate, $Zn(NO_3)_2 \cdot 4H_2O$, confined in mesoporous materials with narrow pore size distributions and different pore diameters (Vycor glass, mesoporous silica). Using a molality based Pitzer model for the calculation of water activity and activity coefficients, the thermodynamic solubility products of the nanocrystals were calculated. Using Eq. (1) and treating γ_{cl} as an adjustable parameter, the data were used to determine values of the surface free energy of the crystal–liquid interface.

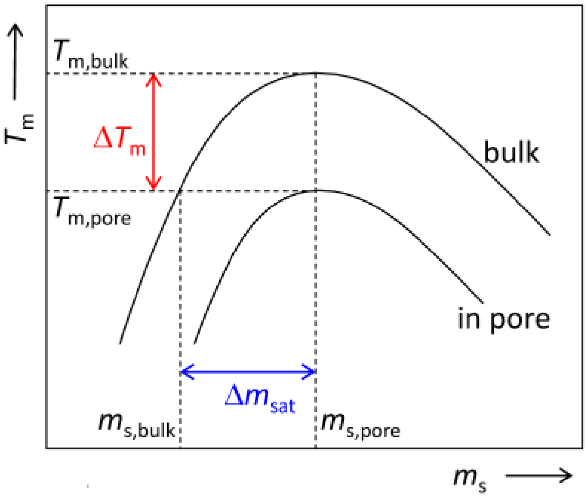


Fig. 1: Solubility curves of a bulk salt hydrate and of nanocrystals (in mesopores). The melting point decrease ΔT_{m} corresponds to a solubility increase Δm_{sat} at the melting temperature of the small crystal.

Reference

[1] M. Steiger, *J. Cryst. Growth* **282**, 470-481 (2005).

OC 30

Solubility measurements and modeling of zinc, lead and iron sulfides at high temperatures and high pressures

Diana Carolina Figueroa, Philip Loldrup Fosbøl, Kaj Thomsen

Department of Chemical and Biochemical Engineering, Center for Energy Resources Engineering (CERE) Technical University of Denmark, Kgs. Lyngby, Denmark

e-mail: difm@kt.dtu.dk

Solubility measurements of sulfides in aqueous solutions are necessary to understand the behaviour of these scaling minerals in geothermal and oil reservoirs. The low solubility levels of Zinc Sulfide (ZnS), Lead Sulfide (PbS) and Iron Sulfide (FeS) make the solubility measurements a challenging task. Consequently existing data are rare and scattered. The aim of this work is to develop a reliable experimental procedure and to measure solubility of sulfides at high temperature and pressures. Additionally the experimental data are used for estimation of the solid-liquid equilibrium using the Extended UNIQUAC model.

The experimental determination of the solubility of ZnS, PbS and FeS is carried out at temperatures up to 200°C and pressures up to 60 bars. The minerals in their pure form are added to ultra-pure water previously degassed with nitrogen. The aqueous solution is prepared in a reduced oxygen atmosphere to avoid the risk of oxidation of sulfide minerals. The solution is kept in an equilibrium cell at constant temperature and pressure with continuous stirring. The concentration of Zn^{2+}, Pb^{2+}, Fe^{2+} and S^{2-} are measured using Inductively Coupled Plasma Optical Emission spectrometry (ICP-OES) as analytical technique.

The solid-liquid equilibria is calculated using the Extended UNIQUAC model. The Extended UNIQUAC model is a local composition model and features several advantages compared to other models when describing the behaviour of aqueous electrolytes systems and it was presented by Thomsen and Rasmussen in 1999 [1]. The model accounts for the dependency of the solubility on pressure and temperature. The pressure parameters were proposed by Villafáfila *et al.* (2005; 2006) [2] on their study on sulfate scaling minerals. The parameter estimation of the model is carried out based on the experimental data produced in our laboratory. The results show that the Extended UNIQUAC model can correlate the solubility data for sulfides within experimental accuracy.

Keywords: Zinc Sulfide, Lead Sulfide, Iron Sulfide, Solid-Liquid Equilibria, Extended UNIQUAC

References

[1] K. Thomsen, P. Rasmussen, Modeling of vapor–liquid–solid equilibrium in gas–aqueous electrolyte systems. *Chem. Eng. Sci*. **54**, 1787-1802 (1999).
[2] A. Villafáfila Garcia, K. Thomsen, E.H. Stenby. Prediction of mineral scale formation in geothermal and oilfield operations using the extended UNIQUAC model: part I. Sulfate scaling minerals. *Geothermics* **34**, 61-97 (2005).

OC 31

Solubility and speciation of neptunium(V) in alkaline, dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions

David Fellhauer, Xavier Gaona, Kathy Dardenne, Marcus Altmaier

Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany, P.O. Box 3640, 76021 Karlsruhe, Germany

e-mail: david.fellhauer@kit.edu

For the long-term safety assessment of nuclear waste repositories, a reliable understanding and thermodynamic description of the principal geochemical processes of actinide elements in aqueous solutions is highly relevant, e.g. regarding solubility behavior, complexation reactions or redox processes. Solubility phenomena strongly control the radionuclide source term, i.e. the maximum amount of dissolved radionuclide species potentially mobilized from the near-field of a repository in the case of water intrusion. Due to its long half-life and abundance in spent nuclear fuel, ^{237}Np is an element of high relevance in this context. In aqueous solutions, the pentavalent oxidation state of Np is thermodynamically stable over a wide range of E_h and pH conditions. The solubility and hydrolysis behavior of Np(V) has been subject of several studies that were mainly performed in NaCl or $NaClO_4$ solutions as background electrolyte. According to a widely accepted chemical model [1], the solubility of Np(V) in dilute to concentrated NaCl-NaOH solutions is controlled by equilibrium reactions between the binary hydroxide solid phase NpO_2OH(am) and the aqueous species $NpO_2(OH)_n^{1-n}$ with n = 0 to 2.

In the last few years, we have performed new solubility experiments with Np(V) in alkaline, dilute to concentrated NaCl [2], $MgCl_2$, and $CaCl_2$ [3,4] solutions which reveal that the current chemical model for Np(V) needs to be extended. The formation of so far not considered ternary M-Np(V)-OH(s) solid phases with M = Na, Ca (e.g. $Ca_{0.5}NpO_2(OH)_2$(s,hyd)) readily takes place under these conditions. Our comprehensive experimental data show that the latter have significantly lower solubilities compared to binary NpO_2OH(am). From the systematic dependence of the solubility of these well-defined solid compounds on pH_m and ionic strength, important information about the Np(V) hydrolysis model and especially the corresponding thermodynamic constants is derived, which help to solve some contradictory discussions on this issue [5]. Furthermore, clear indications for the formation of ternary hydrolysis complexes, $Ca_xNpO_2(OH)_y^{2x+1-y}$, in Ca containing solutions are obtained. From the comprehensive solubility data up to $pH_m = 10$, where hydrolysis of Np(V) is negligible, and additional Vis/NIR and Np-L3 EXAFS spectroscopic investigations of aqueous Np(V) solutions in $MgCl_2$ and $CaCl_2$ solutions, a detailed description of the innersphere chloro complexation of Np(V) is achieved.

In the presentation, the new experimental results and the corresponding thermodynamic equilibrium data (solubility products, complex formation constants, ion interaction parameters derived within both the SIT and Pitzer approaches) are summarized.

References

[1] R. Guillaumont, Th. Fanghänel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, M.H. Rand, (OECD, NEA-TDB), *Chemical thermodynamics vol. 5, update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*, Elsevier, North-Holland, Amsterdam (2003).
[2] V. Petrov, X. Gaona, D. Fellhauer, K.S. Dardenne, N. Kalmykov, M. Altmaier, Abstract No. A1-3, 13th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Migration '11, Beijing, China, 18-23 September, 2011.
[3] D. Fellhauer, J. Rothe, M. Altmaier, V. Neck, J. Runke, T. Wiss, Th. Fanghänel, *Radiochim. Acta* (2016) (DOI 10.1515/ract-2015-2489).
[4] D. Fellhauer, M. Altmaier, X. Gaona, J. Lützenkirchen, Th. Fanghänel, *Radiochim. Acta* (2016) (DOI 10.1515/ract-2015-2490).
[5] V. Neck, *Geochim. Cosmochim. Acta* **70**, 4551-4555 (2006).

OC 32

Solubility of lithium sulfate and the effect of other electrolytes

Julia Sohr, Wolfgang Voigt

TU Bergakademie, Freiberg, Germany

e-mail: julia.sohr@chemie.tu-freiberg.de

Lithium and sulfate ions are natural constituents of brines in salt lakes located in South America, China and Turkey. During processing of these brines by solar evaporation for lithium recovery the lithium component can precipitate as sulfate or in form of a sulfatic double salt with sodium or potassium ions. These precipitations cause lithium losses; in other technological schemes, however, the crystallization of lithium sulfate helps to isolate the lithium component from the other salts. Thus, knowledge of the solubility of lithium sulfate in simple and complex systems is important to adapt the technologies to the requirements by given resources and product quality.

As a contribution to the IUPAC-NIST Solubility Data Series (SDS) data on the solubility of lithium sulfate in aqueous solutions have been collected and evaluated. The compilation comprises 11 data sets of the pure binary system. Moreover, 38 ternary, 28 quaternary, 10 reciprocal and 7 higher systems containing lithium sulfate have been compiled.

This contribution will give a short overview over the data pool and the evaluation process. Recommended values for solubility of lithium sulfate in pure binary as well as higher systems will be presented.

Furthermore, focus will be put on the thermodynamics of dissolution of lithium sulfate in water: On basis of a model from literature [1] activity coefficients and solubility constant of lithium sulfate in pure water can be calculated as a function of temperature. We will investigate and discuss the influence on these activity coefficients due to other electrolytes present in solution.

Reference

[1] H.F. Holmes, R.E. Mesmer, Thermodynamics of aqueous solutions of the alkali metal sulfates, *J. Sol. Chem.* **15**, 495-517 (1986).

OC 33

Solubility phenomena of sparingly soluble fluoride salts in zinc hydrometallurgical systems

Dewen Zeng

College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, Hunan Province, P.R. China

e-mail: dewen_zeng@hotmail.com

The F^{-} ions in aqueous hydrometallurgical systems harms production processes and needed to be removed. One of the economical and efficient processes for removing F^{-} is to precipitate the ions as sparingly soluble salts. As it is well known that some fluoride salts, i.e. CaF_2, MgF_2 and LnF_3, are sparingly soluble in pure water [1]. However, their solubility behaviors become complicated in the presence of a second and (or) third salt in the aqueous solution. The common ion effect on the solubility of the sparingly soluble salts don't work all the time. While $MgCl_2$ increases the MgF_2 solubility by almost 50 times [2], AgF decreases the MgF_2 solubility to undetectable level [3].

In this presentation, available experimental data of the solubility isotherms in the concerned systems $MFx\text{-}MSO_4\text{-}H_2O$, $MF_x\text{-}ZnSO_4\text{-}H_2O$, $MF_x\text{-}H_2SO_4\text{-}H_2O$ (M=Mg, Ca, and La; x=2 or 3) are reviewed. It is found that the solubility data in these systems are so scarce that the CaF_2 solubility in such simple a system $CaF_2\text{-}CaSO_4\text{-}H_2O$ is even unavailable. The effect of salts on the relative apparent activity coefficient of F^{-} ion in some systems are reported. The effect in density of the added salts on the F^{-} ion activity are interpreted in the solution structure aspect.

References

[1] W.F. Linke, A. Seidell, (Eds.). *Solubilities, Inorganic and metal-organic compounds*. American Chemical Society, Washington, DC, 1965.

[2] G.A. Lopatkina, N.L. Antoshkina, T.V.B. Lokhina, N.G. Nikol'skaya, Study of solubility in the magnesium fluoride-magnesium chloride-water system at 25°. *Zhurnal Prikladnoi Khimii* **57**, 2356 (1984).

[3] Sh.T. Talipov, D.A. Abdullaev, M.V. Kirsanova, Investigation of solubility in the system MgF_2-AgF-H_2O at 25°. *Trudy Sredneaziat. Univ., No. 40, Khim. Nauki* **5**, 43-46 (1953).

OC 34

Dissolution-precipitation kinetics of fluoride-bearing minerals in groundwater

Aravinth Subramaniam, Abhas Singh

Department of Civil Engineering, Indian Institute of Technology, Kanpur, U. P., India

e-mail: abhas@iitk.ac.in

Excessive intake of fluoride (F) through drinking water is considered the leading cause for dental and skeletal fluorosis affecting more than 200 million people in India and several parts of the developing world. Fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6) are the typical F-bearing minerals, which upon dissolution release F in groundwater. Precipitation-dissolution kinetics of these minerals under different conditions is poorly understood, especially the role of co-solutes. In this contribution we investigate the extent and rates of transformation of calcium phosphates into fluorapatite, and of gypsum ($CaSO_4$) into fluorite under approximate *in situ* F-contaminated groundwater conditions. Dissolved and solid phase characterization results from complimentary batch and flow-through experiments will be presented, and interpreted using a carefully selected thermodynamic database. Findings from this study will likely benefit remediation of F-contaminated groundwater.

OC 35

Determination of phase equilibria in the quinary $Na,K//SO_4,CO_3,HCO_3 – H_2O$ system at 100°C

Sherali Tursunbadalov[1], Lutfullo Soliev[2]

[1]Department of Chemistry, Faculty of Natural and Applied Sciences, Nigerian Turkish Nile University, Plot 681, Cadastral Zone C-OO, Research & Institution Area, FCT Abuja,Nigeria
[2]Department of General and Inorganic Chemistry, Faculty of Chemistry, Tajik State Pedagogical University, Rudaki 121, Dushanbe, Tajikistan

e-mail: s.tursunbadalov@ntnu.edu.ng

The multicomponent systems compose considerably valuable raw materials of chemical industry and utilization of such kind of systems requires self-consistent and rigorous theoretical background. The preliminary experimental investigations which are performed to understand the systems better; obviously lack particular guides for the multicomponent water-salt systems. As the obtained results from the latter experimental investigations are depicted on the three dimensional spaces; this depiction also gets more complicated as the number of components increases in the system. The need to resort to theoretical investigation of phase equilibria in multicomponent systems was emphasized by G.Tamman [1]. He stresses that "the greater the number of substances in the mixture - the greater the requirements on the experimenter to avoid unnecessary tests. In this case, the only theory shows how; with a minimum number of experiments one can achieve the desired results".

As the simple systems can easily be investigated well traditionally; the study of more complex quaternary and higher component water-salt systems already involve limitations; saturation of system and elimination of phases in the systems. But an incomplete knowledge about the composition of the system is generated in this case. The majority of the parts of the system namely the sections that are excluded from the latter eliminations remain without any elucidations. And regretfully; the results obtained from the latter studies involving eliminations are considered as complete studies of the system. Obviously, the development of more comprehensive and universal methods of investigation of multicomponent water-salt systems is must.

Phase equilibria in the $Na,K//SO_4,CO_3,HCO_3 – H_2O$ system at 100°C were studied by means of “translation method [2,3]”. 39 divariant fields, 43 monovariant curves, 16 invariant points have been determined in the system at 100°C. The first comprehensive closed phase equilibria (phase complex) diagram of system has been constructed. For more clarity, the obtained diagram has been fragmented into divariant co-crystallization fields and trivariant crystallization volumes of 13 individual salts in the system. The “translation method” has been used in investigation of phase equilibria in several multicomponent systems [4-7] so far.

References

[1] G. Tamman, *The Manual on Heterogeneous Equilibria;* ONTI, Khimteoret: Leningrad, 1935 [in Russian].
[2] L. Soliev, Prediction of structure of phase equilibria diagrams of multicomponent water-salt systems using the translation method. Moscow, 28p. *Dep. in VINITI*, 20.12.1987, *No.8990 - V87.*
[3] L. Soliev, Prediction of marine - type multicomponent system phase equilibria by means of translation method. TGPU: Dushanbe, Book I, 2000 [in Russian].
[4] L. Soliev, Sh. Tursunbadalov, Phase equilibria in the $Na,K//SO_4,CO_3,HCO_3-H_2O$ system at 25°C. *Zh. Neorg. Khim.* **53**, 869-875 (2008) [*Russ. J. Inorg. Chem.* **53**, 805-811 (2008)].
[5] L. Soliev, Sh. Tursunbadalov, Phase equilibria in the $Na,K//SO_4,CO_3,HCO_3-H_2O$ system at 0°C. *Zh. Neorg. Khim.* **55**, 1373-1378 (2010) [*Russ. J. Inorg. Chem.* **55**, 1295-1300 (2010)].
[6] L. Soliev, Sh. Tursunbadalov, Phase equilibria in the $Na,K//SO_4,CO_3,HCO_3-H_2O$ system at 50°C. *IOP Conference Series, Mat. Sci & Eng.* **47**, 012050 (2013).
[7] Sh. Tursunbadalov, L. Soliev, Phase equilibria in the $Na,K//SO_4,CO_3,HCO_3–H_2O$ system at 75°C. *J. Solution Chem* **44**, 1626-1639 (2015).

OC 36

Salting out of benzene in water: A consistency evaluation

Alex De Visscher

Department of Chemical and Petroleum Engineering, Schulich School of Engineering, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada

e-mail: adevissc@ucalgary.ca

Data on the salting out of benzene in water is critically evaluated based on solubility data and Henry constant data. It was found that data in NaCl solutions and sea salt solutions can be treated as a single data set. The Setschenow coefficient decreases with increasing salt concentration, and increases with increasing temperature. The data do not allow an evaluation of the interaction between temperature and salt concentration on the Setschenow coefficient. Combining all the data, as well as solubility, Henry constant, and infinite dilution activity coefficient data for benzene in pure water, it is possible to put forward general equations for benzene solubility and derived properties in a range of temperatures (0-60 °C) and salt concentrations (0-360 g kg^{-1}).

Critical evaluation of the Setschenow coefficients of different electrolytes for benzene was based on the Pitzer formalism of assigning interaction parameters assuming no effect of H^+ on the solubility. The data show a high degree of internal consistency, and a fair degree of correlation with interaction parameters published previously for salting out of CO_2.

OC 37

Solid phase formation in ternary aqueous and aqua-organic saline systems

Mikhail Yu. Skripkin[1], Igor V. Zamyatin[2], Artem O. Gorbunov[1], Nikita A. Bogachev[1],
Kim A. Burkov[1]

[1]Saint-Petersburg State University, Saint-Petersburg, Russia
[2]National Mineral Resources University (Mining University), Saint-Petersburg, Russia

e-mail: m.skripkin@spbu.ru

The synthesis of inorganic materials from solutions is one of the modern approaches of material science enabled us to get the desirable compounds with minimum energy expenses and maximum compliance with the Green Chemistry. Therefore the development of methods to predict the composition, structure and crystallization region of solid compounds on the basis of the study of solution properties seems to be rather actual task. In this communication some principal factors that determine the formation of different kinds of solid compounds will be under discussion:

- thermodynamic stability and kinetic inertness of first salvation sphere as the key factor that determines the principal opportunity of double salts formation in the systems containing strongly solvated cations;
- hydrogen bonds effect on formation of solid compounds;
- effect of acidocomplexes stability constants and their ratio on solid phase formation in the systems with competing complexation;
- dielectric permittivity and donor ability of solvent, softness of the solution components as the key factors that determine solubility in aqua-organic saline systems, composition and structure of individual and mixed aqua-organic crystallosolvates and the conditions of their crystallization.

Acknowledgements
This work was supported by RFBR, projects 14-03-01003 and 15-03-05139. Centre for X-ray Diffraction Studies, Centre for Optical and Laser Materials Research and Thermogravimetric and Calorimetric Research Centre of Saint-Petersburg State University Research Park are greatly appreciated for the help in experimental work.

OC 38

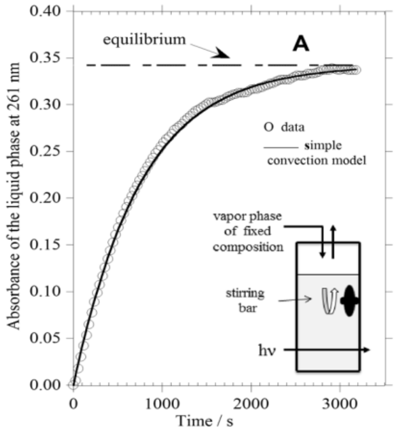
The prediction of equilibrium and the studies of the rate of mass transfer of the solute, toluene, to and from the head space with constant composition to a stirred aqueous phase in a spectrophotometric cell

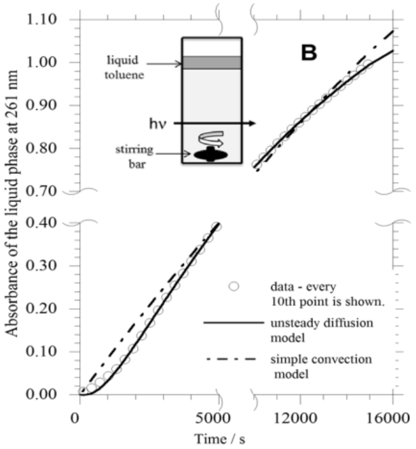
Keith B. Lodge

University of Minnesota Duluth, Chemical Engineering, 1303 Ordean Court, Duluth, Minnesota 55812-3025, U.S.A.

e-mail: klodge@d.umn.edu

Our earlier development of a method for the measurement of fugacity for volatile solutes containing chromophores involved the preparation of a vapor phase with a known composition [1]. This was passed over water in a spectrophotometric cell and stirring (magnetic) was done from the side of the cell; the approach to equilibrium was monitored by recording the absorbance of the liquid at 261 nm — the data were shown to follow a simple convection model that gave rise to: $C_m(t) = C_i + (C_o - C_i)e^{-t/\tau_m}$. Here, $C_m(t)$is the concentration of solute in a well-mixed region within the light beam at time t; $C_i$is the concentration of solute at the gas-liquid interface; $C_o$is the initial solute concentration throughout the liquid; and, $\tau_m = (H - L) / k_c$, where H is the depth of liquid in the cell, Lis the depth of the well-mixed region and$k_c$is the mass transfer coefficient for the concentration-difference driving force. This enables the final equilibrium — see the Fig. A — to be established.





Later we repeated these experiments — and extended them to water solubility and desorption — in a different instrument within which stirring was done from the bottom of the cell. Here, we found that the approach to equilibrium did not necessarily follow the simple convection model — sample data and model fits are shown in the Fig. B for a water solubility experiment. To understand this, we developed an unsteady diffusion model [2] in which a stagnant layer of liquid sits above a well-mixed region below — through this the light beam passes. This leads to the solute concentration in the well-mixed region:

$$C_m(t) = C_i + (C_o - C_i)e^{-t/\tau_m} + \frac{4}{\pi}(C_0 - C_i)\sum_{n=0}^{\infty}\frac{A_n\tau_s(n)}{\tau_s(n) - \tau_m}\{e^{-t/\tau_s(n)} - e^{-t/\tau_m}\}$$

Where $A_n = (-1)^n / (2n + 1)$ and $\tau_s(n) = 4L^2 / (2n + 1)^2\pi^2 D$; here, Dis the diffusion coefficient of the solute toulene. For the data in Fig B, the predicted equilibrium absorbance for the simple convection model turns out to be significantly larger from that for the unsteady diffusion model, which agrees well with other independent experiments. This can appreciated from the longer time behaviour in Fig B. (The data were fitted by a least-squares fitting procedure with$\tau_m$and $\tau_s(0)$the adjustable parameters. The simple convection model is a special case: $\tau_s(0) = 0$.) The analysis here shows: the predicted equilibrium position depends upon having the optimum quantitative description of the system's behaviour. The theory, experiments and results will be described.

References

[1] K.B. Lodge, D. Danso, *Fluid Phase Equilibria* **253**, 74-79 (2007).
[2] K.B. Lodge, *21*st *International Congress of Chemical and Process Engineering*, CHISA 2014, Prague.

OC 39

Liquid-liquid extraction of ethylene glycol from an aqueous solution with 1-hexanol alcohol

H. Ghanadzadeh Gilani, ToubaTaki

Department of Chemical Engineering, Faculty of Engineering, University of Guilan, Rasht, Iran

e-mail: hggilani@guilan.ac.ir

Extraction of Ethylene glycol, which is synthesized from the ethylene oxide hydrolysis, from the aqueous phase according to its wide application in different industries as antifreeze or deicing agent is studied in this survey [1]. Also ethylene glycol is used normally as an aqueous solution of organic inhibitor to avoid formation of gas hydrates formation in natural gas production, transportation, and processing [2].

In this paper, liquid-liquid equilibrium of the ternary system of water+ Ethylene Glycol+ 1-Hexanol alcohol was investigated in three temperatures (T=298.15, 308.15 and 318.15 K) and atmospheric pressure. The cloud point method was used to measure the solubility data and the acidimetric titration and Karl-Fischer methods were used to determine the tie-line data [3]. The investigated ternary system is classified in the LLE systems of type-1 according to the experimental data. The solubility and tie-line data were measured and the ternary diagrams as a function of temperatures are plotted. Also the separation factors were calculated to evaluate the extracting capability of the solvent. In fact the separation factors from the experimental results indicate the possibility of extraction Ethylene glycol by 1-Hexanol alcohol from aqueous phase.

The correlation of the experimental data is done by NRTL model with two values of non-randomness parameter in the mixture (α=0.2 and α=0.3). The new NRTL binary interaction parameters ($\tau_{ij}=a_{ij}/T+b_{ij}$) are optimized by the function fminsearch in our work. Fminsearch is a standard function of MATLAB software. This function is an implementation of Nelder-Mead simplex method. The results demonstrate the capability of this model in simulation of the phase behavior of the related ternary system with the average root mean square deviation values between the experimental and calculated data as an objective function.

Table 1: NRTL binary interaction parameters (aij and bij) and rmsd values for the ternary systems

i-j	**α=0.2**					**α=0.3**				
	a_{ij}	b_{ij}	a_{ji}	b_{ji}	RMSD(%)	a_{ij}	b_{ij}	a_{ji}	b_{ji}	RMSD(%)
1-2	-7231.34	24.83	-3352.5	12.22	0.81	3637.51	-8.29	-93996.7	331.27	0.757
1-3	4726.7	17.15	5543.98	-13.93		1099.61	0.51	-1747.2	6.26	
2-3	869.71	0.65	-7287.47	24.47		51.63	74167.2	1443.93	-1.28	

References

[1] R.Y.M. Huang, Pinghai Shao, X. Feng, W.A. Anderson, *Ind. Eng. Chem. Res.* **41**, 2957-2965 (2002).

[2] A.H. Mohammadi, D. Richon, *Ind. Eng. Chem. Res.* **49**, 925-928 (2010).

[3] H. Ghanadzadeh Gilani, Asan Sh., *Fluid Phase Equilibria* **354**, 24-28 (2013).

OC 40

Solubility and stability of gabapentin anhydrate and hydrate in alcohol + water mixtures

Yan Wang[1,2], Shichao Du[1,2], Junbo Gong[1,2,3]

[1]National Engineering Research Center of Industry Crystallization Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin, China
[2]The Co-Innovation Center of Chemistry and Chemical Engineering of Tianjin, Tianjin University, Tianjin, China
[3]Key Laboratory Modern drug delivery and high efficiency in Tianjin University, Tianjin, China

e-mail: wangyan57@tju.edu.cn

In solution crystallization, the solubility characteristics of a solute have a considerable influence on the choice of appropriate solvents, crystallization method and operating parameters. [1] The solid form (e.g. polymorphs, solvates, co-crystals, salts, and amorphous solids) and crystal morphology can thus be affected, as well as the bioavailability and processability of the product in the manufacturing environment. [2] Therefore, solubility data are of great importance for both theoretical study and industrial application.

The present study is aimed at better understanding the phase behavior and dissolving capacity of anhydrate/hydrate in lower alcohol-water mixtures. Gabapentin, a water-soluble antiepileptic drug, has been selected as the model compound in this work. The anhydrate (form II) presents as rod-like crystals while the monohydrate (form I) turns to be plate-like crystals, which makes it easier to observe the phase transformation process. The physical stability of gabapentin anhydrate/monohydrate at 293.15 K was investigated by slurry experiments. Optical microscopy, scanning electron microscopy, powder X-ray diffraction, and thermogravimetric analysis were used to characterize the solid forms. Isothermal triangular phase diagram was applied for analyzing the phase behavior of three-component systems. During the increase content of water, the solubility of gabapentin reached a maximum at $C_{water} = 0.293$ (mass fraction of water in solution), taking place at point C where the anhydrate and monohydrate are in equilibrium. According to water activity, the corresponding equilibrium constant of the hydration process K_h was calculated as 1.33.

Then, the solubility of the stable form in binary mixtures (water-ethanol and water-methanol) was measured systematically at various temperatures. For gabapentin anhydrate, the solubility increases with water content, and there is a maximum with a certain composition at higher temperatures; for the monohydrate, the solubility decreases with water content, and there is a minimum at lower temperatures. By van't Hoff equation, the transition temperature can be obtained to display temperature dependence of the relative stability between anhydrate/hydrate.

Furthermore, with the purpose of exploring molecular association for gabapentin-water-ethanol mixtures in equilibrium, molecular dynamics simulation study of radius distribution functions and H-bond distribution is presented. Selected results are shown in Figs 1-3.

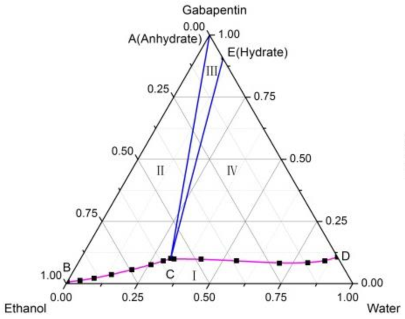


Fig. 1: Ternary Phase diagram

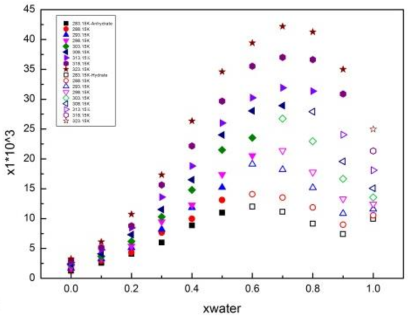


Fig. 2: Solubility in ethanol-water mixture

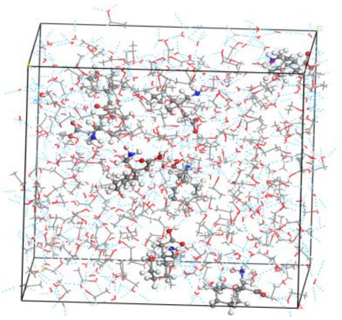


Fig. 3: Molecular association by H-bond

References

[1] J.W. Mulin, *Crystallization*. Butterworth-Heinemann, 2001.

[2] F. Tian, H. Qu, A. Zimmermann, T. Munk, A.C. Jørgensen, J. Rantanen, *J. Pharma. Pharmacol.* **62**, 1534-1546 (2010).

Closing lecture

Stability and change in pieces of art

M. Clara F. Magalhães[1], Joana Almeida[1], Ricardo Santos[1], Heinz Gamsjäger[2]

[1] Department of Chemistry and CICECO, University of Aveiro, P-3810-193 Aveiro, Portugal
[2] Montanuniversität, Lehrstuhl für Physikalische Chemie, 8700 Leoben, Austria

e-mail: mclara@ua.pt

In spite of the human desire to keep forever the pieces of art, whenever they have been kept – buried, inside houses or outdoor in gardens or even in the buildings' façades – they usually change with time. Paintings become darker; pigments, and dyes can fade or change colors; rocks, and minerals metamorphose with time. It is well known the alteration of statues, monuments and buildings' façades as a result of the action of the atmosphere. The deterioration of metal artifacts (*e.g.* copper, bronze, lead) can be a source of information both on the technical aspects of their manufacture as in the changes that occur in their environments. An example are the green patinas that cover copper containing objects, which can be malachite [$Cu_2(CO_3)(OH)_2$], brochantite [$Cu_4(OH)_6(SO_4)$] and other copper(II) sulfates, and even atacamites [$Cu_2Cl(OH)_3$] as is the case in maritime environments [1, 2].

Since pre-history that human beings use paintings as a mean of expression. In the paintings, pigments and binders are applied on a support base. An important characteristic of a traditional pigment is low solubility in solvents and binders. However, slowly they can change their composition and colors with time, as result of possible reactions between the pigments themselves, and between those and their surrounding environment. The reactions that can happen depend on the materials (binders, pigments and support base) but also in the environment (*e.g.* atmosphere composition, humidity, temperature, pressure) where they have been kept. Changes happen because water is present and the materials slowly tend to originate more stable phases under the physical-chemical conditions of their neighbourhood.

The presence of humans increase the concentrations of carbon dioxide and sulfur containing species present in the atmosphere as well as its humidity. The materials react more or less slowly, with the increasing amounts of carbon dioxide, sulfur containing species and humidity present in the atmosphere, producing carbonates and sulfates.

Thermodynamic parameters show which solid phases will be stable under the atmospheric conditions (temperature, pressure, atmosphere composition – water vapor and carbon dioxide partial pressures, etc.) the pieces of art are being subjected as well as the local conditions promoting the changes. The evaluation of the published data for lead(II) carbonates allow the understanding of the conditions that promote the degradation of pigments containing lead, as red lead (minium, Pb_3O_4), yellow massicot (PbO), white lead [$Pb_3(CO_3)_2(OH)_2$] whose darkening of the colors can be explained by the formation of black plattnerite (PbO_2) or grey galena (PbS), and the fading by the formation of white solids as anglesite ($PbSO_4$), cerussite ($PbCO_3$) or carbonatehydroxides with the composition and structure of plumbonacrite [$Pb_5(CO_3)_3O(OH)_2$] and hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] [3].

References

[1] D. de la Fuente, J. Simancas, M. Morcillo, *Corrosion Science* **50**, 268-285 (2008).
[2] A.H. Zittlau, Q. Shi, J. Boerio-Goates, B.F. Woodfield, J. Majzlan, *Chemie der Erde* **73**, 39-50 (2013).
[3] F. Vanmeert, G. Van der Snickt, K. Janssens, *Angewandte Chemie Int. Ed.* **54/12**, 3607-3610 (2015).

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Poster communications

P 1

Energy generation through waste water as a remedy for better governance: A case study of the City of Lagos, Nigeria

Timothy Ajayi

Department of Science Laboratory Technology, Ogun State Institute of Technology, PMB 2005 Igbesa, Ogun State, Nigeria

e-mail: ajayi.timothy@ogitech.edu.ng

Introduction and Objectives

As Nigeria's economic capital and commercial nerve centre, the city of Lagos is undergoing speedy urbanization. With an estimated population of over seventeen million people, Lagos is one of the world's fastest growing cities. One of the prominent natural endowments that has borne the brunt of this rapid expansion is the Lagos Lagoon, a water body that has been used for sewage disposal for more than half a century. The large volume of sewage deposited in the lagoon on a daily basis has escalated due to the rapid growth in the city's population.

Besides adding beauty to the city, the Lagos Lagoon is a veritable source of seafood for Lagosians. As is the case with other sewage-rich, densely-populated cities, the city of Lagos has not fully utilized its bounteous sewage resources to upscale its energy supply needs. Instead, the inhabitants of the city keep contaminating the lagoon. The thrust of this paper is to explicate the repercussions of wanton sewage disposal into the Lagos Lagoon and to highlight the potential which Lagos has to generate massive energy from sewage waste in order to meet its energy challenges and ensure better governance.

Methodology and Approaches

From ten separate stations across the Lagos Lagoon, water samples were collected and analyzed to ascertain the existence of pathogenic entities using the techniques of sedimentation, microscopy and culture. These pH levels and Biochemical Oxygen Demand (BOD) of the samples were tested using the pH meter and BOD test apparatus correspondingly. The average number of sewage tankers who offload waste on a daily basis in all the sewage disposal sites were recorded. This was used to calculate the average daily sewage waste volume disposed.

Analysis and Results

The analysis showed that pathogenic organisms like hookworms, *Kleibsiella spp*., *Salmonella spp.*, *Escherichia coli*, *Giardia intestinalis* and *Ascaris lumbricoides* were present. Also, the test revealed a pH of 7.9-8.5 and a BOD level of 95-225mg/l at 20^0C for 5 days. The general outcome is that on the average, tankers in Lagos deposit 720,000 litres of sewage wastes (mostly faecal sludge), and sixty-six per cent of these goes directly or indirectly into the Lagos Lagoon.

Conclusions and Recommendation

This paper shows that sewage disposal into the Lagos Lagoon has made the water body ecologically unhealthy for aquatic plants and animals. It has also decreased the visual appearance of the environment. Further, this cruel practice has exposed some persons that come in contact to the lagoon's waters to pathogenic infections. Extant studies have pointed to the fact that sewage waste is a key energy source, with 1 kilogramme of dry faecal sludge having a calorific value of 17.3 millijoule. The implication of this discovery is that with a daily average of 720,000 litres of faecal sludge disposal into the lagoon, Lagos has what it takes to meet its growing energy demand. The absence of steady energy supply has reduced the quality of life and governance in the city. Thus, the onus lies on government to effectually surmount the energy crisis and improve the life of the denizens. This paper strongly recommends the dynamic use of faecal sludge to save the Lagos Lagoon from sewage pollution and upscale energy supply in Lagos.

Key words: sewage, energy, water, lagoon, sewage tanker, governance panacea.

P 2

ThermAc - a collaborative project on aquatic chemistry and thermodynamics of actinides at elevated temperature conditions

M. Altmaier[1], F. Brandt[5], V. Brendler[2], I. Chiorescu[6], E. Colàs[7], H. Curtius[5], F. Endrizzi[1], C. Franzen[2], X. Gaona[1], M. Grivé[7], S. Hagemann[4], C. Koke[3], D.A. Kulik[8], S. Krüger[6], J.-Y. Lee[1], M. Maiwald[3], G.D. Miron[8], P.J. Panak[3], A. Skerencak-Frech[3], R. Steudtner[2], T. Thoenen[8], S. Tsushima[2]

[1]Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany, P.O. Box 3640,
76021 Karlsruhe, Germany
[2]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology (HZDR-IRE), Dresden, Germany
[3]University of Heidelberg, Institute for Physical Chemistry, Heidelberg, Germany
[4]Gesellschaft für Reaktor und Anlagensicherheit (GRS), Braunschweig, Germany
[5]Jülich Research Center, Institute of Energy and Climate Research (IEK-6), Jülich, Germany
[6]Technische Universität München, Theoretical Chemistry, Munich, Germany
[7]Amphos21 Consulting, Barcelona, Spain
[8]Paul Scherrer Institut, Laboratory for Waste Management (PSI-LES), Villigen, Switzerland

e-mail: marcus.altmaier@kit.edu

The ThermAc project is extending the chemical understanding and available thermodynamic database for actinides, long-lived fission products and relevant matrix elements in aquatic systems at elevated temperatures. To this end, a systematic use of estimation methods, new experimental investigations and quantum-chemistry based information is used. ThermAc has started in March 2015 and is projected for three years, running until 28.02.2018. The project is funded by the German Federal Ministry for Education and Research (BMBF) and is coordinated by KIT-INE.

The ThermAc project is developed with the aim of improving the scientific basis for assessing nuclear waste disposal scenarios at elevated temperature conditions. Adequate scientific tools must be available to assess the related chemical effects and their impact upon safety. A clear focus of ThermAc is on long-lived actinides in oxidation states III, V and VI, with selected fission products and important redox controlling matrix elements like Fe also receiving attention. Tetravalent actinides and detailed investigations of redox processes are excluded from the current ThermAc work programme. ThermAc mainly addresses the temperature range from ~5°C up to ~90°C, focusing on systems at low or intermediate ionic strength. Chemical analogs for the actinide elements will be used, especially in order to gain information on solid phase transformation processes. Ion-interactions are treated with the Specific Ion Interaction Theory (SIT), in agreement with the approach favored by the NEA-TDB project. Quantum chemical calculations are used to support the interpretation of experimental findings, and establish a fundamental understanding of chemical effects on a molecular level.

Within the scope of ThermAc, a significant impact can be realized within a strong collaborative and integrated concept with the following strategic components:

(1) Systematic use of estimation methods for thermodynamic data and model parameters.
(2) Comprehensive experimental validation of the estimations.
(3) Fundamental studies for improved process understanding of actinide chemistry at elevated T.
(4) Comprehensive critical evaluation of the work performed within (1-3).

A key result from the comparison of predictions based upon estimation methods with new experimental data derived within ThermAc will be the assessment of the use of estimations methods to set up a workable thermodynamic database for elevated temperatures with high applicability to nuclear waste disposal issues. In this context it will be clarified, to which extent systems will remain critical with regard to available thermodynamic data, and which relevant processes at elevated temperatures are still not sufficiently understood.

Acknowledgement: This project has received funding from the German Federal Ministry for Education and Research (BMBF). KIT-INE is working under the contract 02NUK039A.

P 3

A state-of-the-art report within NEA-TDB to assess modeling and experimental approaches in aqueous high ionic-strength solutions relevant for nuclear waste disposal applications

OECD/NEA Thermochemical Database Project (TDB)

M. Altmaier[1], D. Costa[2], A. Felmy[3], H. Moog[4], R. Pabalan[5], M. Ragoussi[2], D. T. Reed[6],
W. Runde[7], P. Thakur[8], W. Voigt[9]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany
[2]OECD Nuclear Energy Agency, Boulogne-Billancourt, France
[3]Washington State University, Pullman WA, USA
[4]Gesellschaft für Anlagen- und Reaktorsicherheit (GRS), Braunschweig, Germany
[5]U.S. Nuclear Waste Technical Review Board, Arlington VA, USA
[6]Los Alamos National Laboratory, 1400 University Drive, Carlsbad NM, 88220, USA
[7]Los Alamos National Laboratory, Los Alamos NM, 87545, USA
[8]Carlsbad Environmental Monitoring & Research Center, NMSU, Carlsbad NM, USA
[9]Technical University of Freiberg, Freiberg, Germany

e-mail: marcus.altmaier@kit.edu

Within the scope of the OECD Nuclear Energy Agency (NEA) Thermochemical Database (TDB) Project, the preparation of a State of the Art Report (SOAR) to assess the modeling and experimental approaches used to describe high ionic-strength solutions is a current activity. This state of the art report builds on past NEA-TDB documents [1] and focuses on ionic strengths $I \geq 3$ M where the Pitzer formulation [2,3], rather that the SIT approach, is recommended and usually applied. The focus of this SOAR update is on the nuclear waste disposal aspects that apply to repository concepts in bedded and domed rock salt formations, although there is also relevance to other geologic disposal concepts where transient high ionic-strength aqueous conditions can exist. This SOAR assessment activity is the first step in the development of a comprehensive high quality and self-consistent Pitzer data set that can describe the aqueous actinide and brine chemistry for all predicted repository conditions to address low-probability brine-inundation scenarios that are a necessary part of the safety case for a nuclear waste repository in salt [4].

The aqueous solution properties treated within the Pitzer approach that pertains to a nuclear waste repository in salt is divided into different categories: (i) “Oceanic” for the main components of high ionic-strength brine including interactions of main components with carbonate, (ii) “Radionuclide/actinide” for the key radionuclides (and their analogs) and their interactions with main inorganic and organic ligands that need to be addressed to support the safety case, and (iii) “Others” including selected non-radioactive elements of high relevance like iron or lead. The vast majority of the available literature deals with the brine chemistry associated with “oceanic” systems (~1000 species-specific) and this remains a very active area of research for a number of reasons outside of the nuclear repository application. For the radionuclide/actinide data set, there are new data reported for all the key oxidation states of the actinides but there are significantly less literature publications (~65) on this key topic. There is especially a significant lack of temperature-variable data for the radionuclide/actinide data set as well as ternary species and a number of gaps exist in current database applications. A critical assessment of these key data gaps will be provided.

References

[1] Allard *et al. Modelling in Aquatic Chemistry*. OECD Publications, 724 pp., ISBN 92-64-15569-4, 1997.
[2] K.S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268-277 (1973).
[3] K.S. Pitzer, Ion interaction approach: Theory and data correlation. Chapter 3 of *Activity Coefficients in Electrolyte Solutions*. 2nd Edition. Pitzer, 152709 K.S., ed. Boca Raton, Florida: CRC Press. 1991.
[4] D.T. Reed, M. Altmaier (eds.), *Proceedings of the Third International Workshop on Actinide and Brine Chemistry in a Salt-Based Repository (ABC-Salt III),* Los Alamos National Laboratory Report LA-UR-15-21114, Los Alamos, NM, USA, 2015.

P 4

Solubility control of CNT by block copolymer surfactant both in solution and in solid

Kyung-Youl Baek

Center for Materials Architecturing, Korea Institute of Science and Technology (KIST), 39-1 Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Korea

e-mail: baek@kist.re.kr

Carbon nanotubes (CNT) was modified by P3HT-PMMA block copolymer through pi-pi stacking interaction between CNT and P3HT block segment to give stable dispersion in common organic solvents because of the other block PMMA segment. The PMMA coated CNT was then blended with P(VDF-TrFE) (70:30 mol%) to obtain polymer nanocompositesby solution casting process, where the PMMA block segments showed exceptional solubility with PVDF based polymers. Obtained polymer nanocomposites showed enhanced electrical characteristics, as nanocomposites near the threshold of the transition between P(VDF-TrFE) insulatorand CNT conductor revealed great improvement of electrical conductivity up to 10^{-6} S/cm at 1 KHz.

P 5

Thermodynamic models for determination of solubility of Alloxan in various solvents at different temperatures

Shipra Baluja, Kapil Bhesaniya

Physical Chemistry Laboratory, Department of Chemistry, Saurashtra University, Rajkot-360005 (Gujarat), India

e-mail: shipra_baluja@rediffmail.com

The solubility of Alloxan in methanol, ethanol, ethane 1, 2 diol, water, acetone and tetrahydrofuran was measured by gravimetric method over a temperature range (293.15 to 323.15) K at atmospheric pressure. The solubility increases non linearly with temperature in all the studied solvents. The solubility of alloxan is found to increase nonlinearly with temperature. Further, in protic solvents, solubility is maximum in methanol and minimum in ethane 1, 2 diol whereas in the selected non protic solvents, solubility is greater in tetrahydrofuran than in acetone. The experimental solubility data were correlated with temperature by modified Apelblat and Buchowski-Ksiazczak λh equations. Some thermodynamic parameters such as dissolution enthalpy, Gibb’s free energy, and entropy of mixing have also been calculated. The evaluated thermodynamic parameters are found to be positive. The positive enthalpy and Gibb’s free energy indicate endothermic and spontaneous dissolution of compounds. The positive entropy suggests entropy-driving dissolution process.

Keywords: Alloxan, solubility, Apelblat equation, Buchowski-Ksiazczak equation, thermodynamic parameters.

P 6

Solubility and solution thermodynamics of hippuric acid in various solvents from 298.15 K to 328.15K

Shipra Baluja, Elham Abdullah Mo Alnayab, Asmita Hirapara

Physical Chemistry Laboratory, Department of Chemistry, Saurashtra University, Rajkot-360005 (Gujarat), India

e-mail: shipra_baluja@rediffmail.com

The solubility of hippuric acid in methanol, ethanol, 1-propanol, 1-butanol, 1,4-dioxane, chloroform, dimethylformamide and tetrahydrofuran was measured by gravimetric method over a temperature range (298.15 to 328.15) K at atmospheric pressure. The solubility of hippuric acid is found to increase nonlinearly with temperature. Further, in alcoholic solvents, solubility is maximum in methanol and minimum in 1-butanol whereas in non-alcoholic solvents, solubility is greater in dimethylformamide and minimum in chloroform. The experimental solubility data were correlated with temperature by modified Apelblat and Buchowski-Ksiazczak λh equations. The experimental data and model parameters would be useful for optimizing the process of purification. Some thermodynamic parameters such as dissolution enthalpy, Gibb’s free energy, and entropy of mixing have also been calculated by Van’t Hoff analysis.

Keywords: Hippuric acid, solubility, Apelblat equation, Buchowski-Ksiazczak equation, thermodynamic parameters.

P 7

NMR study of the structural-dynamic characteristics of the ternary system CsCl-LiCl-D_2O in the interval from 25°C to the freezing temperature

Valeriie E. Baranauskaite, Olga N. Pestova, Andrey Yu. Efimov

Saint-Petersburg State University, Chemistry Institute, 198504, Saint-Petersburg, Universitetskiy av., 26. Russia

e-mail: valeriiebar@gmail.com

Multicomponent aqueous electrolyte solutions are characterized by wide diversity of physical-chemical properties, thus and so the study of formation mechanisms and conditions of joint compounds in these systems is a crucial task. Variety of properties of such systems include hygroscopicity, high solubility and heat capacity, low freezing temperatures, and formation of joint compounds. Owning to these properties aqueous solutions are used in refrigerating engineering. Besides, the system under study is a model system, due to the different nature of the salts included: chaotropic CsCl and kosmotropic LiCl. The formation of joint compound goes by the structurally forced embedding mechanism. [1]

The results of investigation of suchlike systems with NMR spectroscopy method allow one to receive a notion of nearest surrounding of the ions and of the system structure on the whole, since the NMR method is sensitive to the appearance of irregularity in the solution. Discrepancy between nature of the salts reflects in their different influence on the water molecules mobility. Thus it's interesting to reveal dominant influential in the joint solution. Temperature studies NMR are suitable for the determination of dominant salt.

By applying of NMR method we received ^{2}D, ^{7}Li, ^{133}Cs spin-lattice (T1) and spin-spin (T2) relaxation times (sec), shifts (ppm) for the samples with constant ratio CsCl:LiCl = 1:2, at different concentrations. We refined freezing points of these solutions, and deduced dependency of the velocity of the magnetic relaxation from the temperature in the interval from 25°C to the freezing point at various concentrations.

Structural-dynamic changes with concentration and irregularity occurrence as the temperature effect are analyzed. Acquired structural-dynamic parameters for the ternary system under study are compared with the ones for the binary systems of CsCl-H_2O, and LiCl-H_2O. The dominant influence of the component is determined.

Reference

[1] O.N. Pestova, V.E. Baranauskaite, M.K. Khripun, The formation of double salts in the system LiCl-CsCl-H2O. X-ray analysis. *Rus. J. Gen. Chem.* **86**, ISSN/ISBN: 1070-3632. In print.

P 8

THEREDA – The thermodynamic reference database for a nuclear waste disposal in Germany

Frank Bok[1], Helge C. Moog[2], Marcus Altmaier[3], Wolfgang Voigt[4], Tres Thoenen[5]

[1]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology
[2]Gesellschaft für Anlagen- u. Reaktorsicherheit (GRS) mbH
[3]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal
[4]TU Bergakademie Freiberg, Institute of Inorganic Chemistry
[5]Paul Scherrer Institute, Laboratory for Waste Management

e-mail: f.bok@hzdr.de

The disposal of nuclear waste including the assessment of long-term safety is still an open question in Germany. In addition to the still pending decision about the repository host rock (salt, granite, or clay) the basic necessity of a consistent and obligatory thermodynamic reference database persists. Such a database is essential to assess potential failure scenarios accurately and to make well-founded predictions about the long-term safety. Specific challenges are comprehensive datasets covering also high temperatures and salinities. Against this background, available databases do not suffice and are limited in their use, partly because of high restrictions and resulting incompleteness of reactions. Other databases rely on heterogeneous and therefore inconsistent data leading to incorrect model calculations. Due to these deficiencies THEREDA, a joint project of institutions leading in the field of safety research for nuclear waste disposal in Germany and Switzerland, was started in 2006.

THEREDA contains a relational databank whose structure has been designed in a way that promotes the internal consistency of thermodynamic data. Data considered cover the needs of Gibbs Energy Minimizers (ChemApp) and Law-of-Mass-Action programs (Geochemist's Workbench, EQ3/6, PHREEQC) alike. Parameters for a variety of models describing interactions in mixed phases are included. Namely the Pitzer parameters to describe activity coefficients of hydrated ions and molecules are considered. Both thermodynamic and interaction parameters can be described by temperature functions.

THEREDA offers evaluated thermodynamic data for many compounds (solid phases, aqueous species, or constituents of the gaseous phase) of elements relevant according to the present state of research. In particular, all oxidation states expected for disposal site conditions are covered.

Ready-to-use parameter files are created from the databank in a variety of formats (generic ASCII type, and formats required by the geochemical speciation codes) and offered to the users. They are also used for internal test calculations – one essential element of the quality assurance scheme. The results are documented and provided to the users.

THEREDA is accessible via internet through www.thereda.de. This is not only a portal to the database, but shall also serve as an information and discussion platform on issues concerning the database. Thus we are confident to generate helpful feedback from the anticipated user community.

P 9

Liquid extraction of rare earth metals with ionic liquid solvents: Modeling with COSMO-RS and experimental verification

Frank Eckert[1], Mariusz Grabda[2,3], Dmytro Kozak[2], Takashi Nakamura[2], Sylwia Oleszek[2,3], Mrutyunjay Panigrahi[2], Etsuro Shibata[2]

[1]COSMO*logic* GmbH & Co. KG, Burscheider Str. 515, 51381 Leverkusen, Germany
[2]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan
[3]Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland

e-mail: eckert@cosmologic.de

The recovery of rare earth elements from waste streams is of great importance from the viewpoint of securing resources. Nd and Dy are some of the most technology-critical rare earths, as they are widely used in permanent magnets and are present in a number of electronic devices. We proposed a new recycling process of waste magnet scrap which can selectively extract the rare earth elements. Because of their unique physicochemical and electrochemical properties, the use of ionic liquids (ILs) constitutes an interesting alternative to current recycling technologies. ILs are liquid salts composed solely of cations and anions. Their properties can be tailored by screening appropriate cation-anion combinations. In this study, the most effective IL extraction solvents for NdF_3 and DyF_3, as well as $NdCl_3$ and $DyCl_3$ were determined with COSMO-RS theory [1]. The computational COSMO-RS screening was performed over 4400 (for the chlorides) and over 900 (for the fluorides) hydrophobic ILs. Considering the calculated physicochemical properties of ILs containing these specific ions, the most effective IL extraction solvents for liquid-liquid extraction of the salts were proposed. In addition, extraction experiments were performed, which confirmed the high extraction efficiency of the ILs that were chosen based on the COSMO-RS predictions [2].

Keywords: extraction; technology-critical elements; ionic liquids; COSMO-RS

References

[1] A. Klamt, *J. Phys. Chem.* **99**, 2224 (1995); F. Eckert, A. Klamt, *AIChE J.* **48**, 369 (2002); A. Klamt, F. Eckert, W. Arlt, *Ann. Rev. Chem. Biomol. Eng.* **1**, 101 (2010).

[2] M. Grabda, M. Panigrahi, S. Oleszek, D. Kozak, F. Eckert, E. Shibata, T. Nakamura, *Fluid Phase Equilibria* **383**, 134 (2014); M. Grabda, S. Oleszek, M. Panigrahi, D. Kozak, F. Eckert, E. Shibata, T. Nakamura, *Comp. Theor. Chem.* **1061**, 72 (2015); M. Grabda, S. Oleszek, M. Panigrahi, D. Kozak, F. Eckert, E. Shibata, T. Nakamura, *AIP Conference Proceedings* **1702**, 190004 (2015).

P 10

Radionuclide source term estimations for generic nuclear waste disposal options within the ENTRIA project

David Fellhauer, Vanessa Montoya, Julian Schepperle, Volker Metz, Marcus Altmaier, Horst Geckeis

Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany
P.O. Box 3640, 76021 Karlsruhe, Germany

e-mail: david.fellhauer@kit.edu

ENTRIA is an interdisciplinary project funded by the *German Federal Ministry of Education and Research* (BMBF) where scientist from various academic disciplines (e.g. physical, applied and social science) jointly evaluate criteria for a future decision-making of different disposal options for nuclear waste in Germany. A subtask of *ENTRIA* focuses on a comparison of the risks that different, generic (i.e. non-site specific) disposal options may pose: namely the final disposal in deep geological formations (i) with and (ii) without the intention and consequent arrangements for a potential retrieval of the waste, respectively, as well as (iii) the long-term interim storage in engineered facilities at the surface. As a consequence of the decision to ultimately phase out nuclear power in Germany, the identification of a safe disposal option for radioactive wastes comes more and more into focus. The commission for high level waste disposal implemented by the German government in 2014 is expected to soon provide recommendations for a subsequent site-selection process. It is apparent that an appropriate solution, which is accepted by a major part of the public, will have to be an unbiased balance of multiple aspects, and goes far beyond mere technical answers.

In this contribution, first results of a comparative assessment of a potential release of radionuclides from the generic repository options defined in *ENTRIA* into the geosphere via the water pathway are presented – under the presumption that water intrusion takes place in a future event. Principal geochemical parameters (e.g. redox conditions, pH and salinity of intruding solutions) that are expected to be representative for the generic repository systems on the long-term are evaluated. Based on that, source terms for relevant radionuclides are estimated, i.e. robust upper-limit values of the aqueous radionuclide concentration in the vicinity of the waste canisters (near-field). For most of the radionuclides considered here, in particular the highly radiotoxic actinide elements like plutonium, the free concentrations in aqueous solutions are determined from the solubility limits using reliable experimental data and quality assured thermodynamic constants and parameters (as summarized e.g. in recent reviews of the NEA-TDB or the THEREDA project). The obtained data serve as input parameters for reactive transport models implemented in the interface PHREEQC / Comsol Multiphysics® (iCP) to further assess a potential migration into the far-field of the emplacement waste.

Acknowledgements
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P 11

A new technique for studying vapour-liquid equilibria of multicomponent systems

Federico M. Ferrero Vallana[1], Lynette A.M Holland[2], Kenneth R. Seddon[1]

[1]QUILL, School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Belfast, BT9 5AG, UK
[2]Procter & Gamble London Innovation Centre, Whitehall Lane, Egham, Surrey, TW20 9NW, UK

e-mail: fferrerovallana01@qub.ac.uk

Spectroscopic techniques have been recognised as important tools for monitoring and quantifying gaseous chemical species. Since the 1990s, high precision, multi-species analyses of trace gases in clean air (such as the greenhouses gases: CO_2, CH_4, N_2O and CO) have been performed by Fourier transform infrared (FT-IR) spectroscopy [1]. For example, this technique has been used for the analysis of non-regulated vehicular emissions, the observation of volcanic HCl/SO_2 gas ratios [2], and for the evaluation of volatile organic compound emissions from tropical biomass burning [3].

The sensitivity of FT-IR spectroscopy depends upon the path length and the design of the cell and the detector, allowing detection of species in concentrations as low as parts per billion [4]. This technique also provides evidence upon the interaction between gas-phase species [5].

Here, FT-IR spectroscopy has been used for quantifying the equilibria between gas-phase and liquid-phase species, using ionic liquids as the solvent, since they make no significant contribution to the gas phase [6]. The application of this technique for the quantification of the gas-phase species, and the observed deviations from Raoult's law for a number of selected systems, are also reported.

In the study of vapour-solid or vapour-liquid equilibria vapour pressure is a thermodynamic property of fundamental importance [7]. There are many manometric techniques for measuring vapour pressure described [8], but the isoteniscope [9] and the Reid method [10] are the most commonly used methods for measuring its temperature dependence. The major limitations of these techniques are that (a) they will not detect pressures below 100 Pa, and (b) they provide no information about gas phase speciation and interactions for multicomponent mixtures. Modern improvements in techniques now allow accurate measurements of vapour pressures as low as 1 Pa [4], but still give no information about the nature of the gaseous species. For the study of vapour-liquid equilibria of multicomponent systems, it is essential to quantify the individual species in the gas-phase, and their partial pressures. Here [11] we report a method which can discriminate the contribution of each component to the total vapour pressure of a mixture, and study this as a function of liquid-phase composition and temperature. Its performance has been validated using two standards (naphthalene and ferrocene), and a Raoult's plot surface of a ternary system is reported as proof-of-principle.

References

[1] M.B. Esler, D.W. Griffith, S.R. Wilson, L.P. Steele, *Anal. Chem.* **72**, 206-215 (2000).
[2] D. Richter, M. Erdelyi, R.F. Curl, F.K. Tittel, C. Oppenheimer, H.J. Duffell, M. Burton, *Opt. Laser Eng.* **37**, 171-186 (2002).
[3] T. Karl, T.J. Christian, R.J. Yokelson, P. Artaxo, W.M. Hao, A. Guenther, *Atmos. Chem. Phys.* **7,** 5883-5897 (2007).
[4] P.L. Hanst, S.T. Hanst, *Gas measurement in the fundamental infrared region*; Oriel: Bellingham, WA, USA, 1993.
[5] Y. Maréchal, *J. Chem. Phys* **87**, 6344-6353 (1987).
[6] M. Freemantle, *An introduction to ionic liquids*; Royal Society of chemistry: Cambridge, 2010.
[7] J. Barker, *Aust. J. Chem.* **6**, 207-210 (1953).
[8] B. Vodar, B.L. Neindre, J.P. MacCullough, *Experimental Thermodynamics: Experimental Thermodynamics of Non-Reacting Fluids*; Elsevier Science & Technology: London, 1975.
[9] *Annu. Book ASTM Stand. Part* **24**, 2879-2875 (1979).
[10] *Annu. Book ASTM Stand. Part* **23**, 323-379 (1979).
[11] F.M. Ferrero Vallana, L.A.M. Holland, K.R. Seddon, *Aust. J. Chem.* 2016, Submitted.

P 12

Building a humic-metal binding constants database

Montserrat Filella[1], Wolfgang Hummel[2]

[1]Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland
[2]Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

e-mail: montserrat.filella@unige.ch, wolfgang.hummel@psi.ch

The fraction of natural organic matter more refractory to degradation, often known as fulvic and humic compounds, plays a decisive role in trace element behaviour in environmental systems. For this reason, a lot of research has been devoted to its characterization as well as to the determination of binding constants to quantify its interaction with trace elements.

However, in spite of the effort deployed, the difficulties encountered when trying to compare complexation constants reported in the literature or to find constant values for less studied elements remain well-known problems. The reason is that our ability to measure and interpret the complexation equilibria of humic substances is severely constrained by their ill-defined nature that hinder the application of the experimental and interpretation methods usually applied in the field of stability constant determination.

Moreover, no systematic compilation of published data exists. For this reason, we have undertaken the gathering of all data published on the complexation of trace elements with humic substances over the past 60 years.

Our ultimate goal is the critical analysis and the interpretation of all existing data with the objective of providing a robust framework for further research as well as a useful tool for practical applications.

The project started in January 2009 with the collection of publications in electronic form for subsequent information extraction by members of the project. Currently this collection comprises some 950 articles. So far, a first spin-off of the project has been the elaboration of recommendations concerning quality assurance issues.

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P 13

Direct Red 28 adsorption on Amosil and *Avena sativa L.* – mass transfer and kinetics modelling on the solid/solution interface

Nedyalka Georgieva, Zvezdelina Yaneva

Chemistry Unit, Department of Pharmacology, Animal Physiology and Physiological Chemistry, Faculty of Veterinary Medicine, Trakia University, Students Campus, 6000 Stara Zagora, Bulgaria

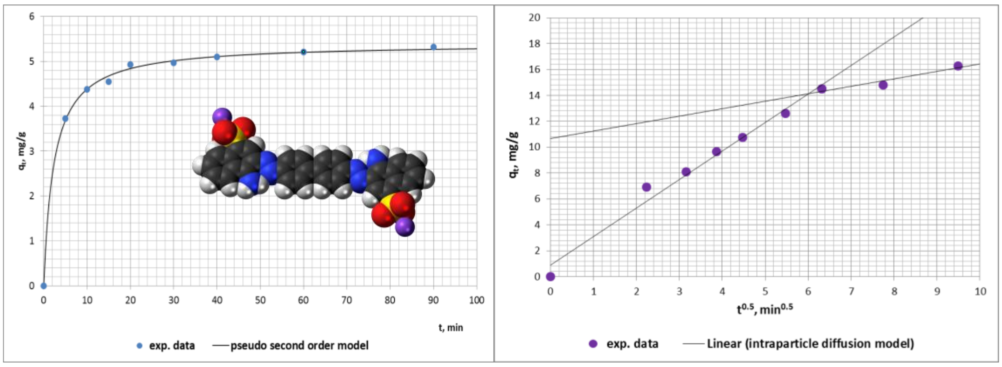
e-mail: z.yaneva@abv.bg

Adsorption kinetics is a key issue for a successful sorbent selection and the proper design of batch and fixed-bed adsorption systems.

The aim of the present study was to determine the kinetics, mass transfer and diffusion coefficients and to establish the rate-controlling mechanism/s during Direct Red 28 adsorption on Amosil and *Avena sativa L.* biomass.

The kinetic experiments were conducted in a standardized batch adsorber. Dye concentrations were determined spectrophotometrically with UV/VIS DR 5000 spectrophotometer (Hach Lange, Germany) at 498 nm. Five kinetics (pseudo-second order, Blanchard, Avrami, Ritchie, power function models) and two diffusion (intraparticle diffusion and Boyd's) mathematical models were applied to the experimental data. To confirm the best-fitting model(s), error analyses were conducted. The linear and non-linear regression analyses were done by the software Origin 9.1 (OriginLab Corporation) and XLStat for Excel.

The integrative comaparative analyses of the values of the predicted model parameters, coefficients and error finctions established that the intraparticle diffusion model best represented the experimental results of the dye sorption on the dried *Avena sativa L.* biomass, while for the system Direct Red 28/Amosil the kinetics behaviour was the most appropriately described by both the pseudo-second and Blanchard's models.



A. **B.**

Fig. 1: Mathematical modelling of the kinetics of Direct Red 28 sorption on: **A.** Amosil by the pseudo-second order model; **B.** *Avena sativa L.* by the intraparticle diffusion model.

The Boyd's effective intraparticle diffusion coefficient (D_i) characterizing the dye sorption on Amosil was significantly lower as compared to that for the system Direct Red 28/*Avena sativa L.* biomass. According to the low values of the *Bi* number ($Bi < 0.5$), the mass transfer resistance for both systems was concentrated on the mass transfer surface fluid/solid phase. Thus, probably the adsorption process was controlled predominantly by external mass transfer. However, the role of chemisorption, especially for the system Direct Red 28/*Avena sativa L.* biomass could not be neglected.

Key words: adsorption, kinetics modelling, mass transfer modelling, Direct Red 28, Amosil, Avena sativa L. biomass

P 14

Synthesis and properties of a new Betti base

Nedyalka Georgieva[1], Zvezdelina Yaneva[1], Svetlana Simova[2]

[1]Chemistry Unit, Department of Pharmacology, Animal Physiology and Physiological Chemistry, Faculty of Veterinary Medicine, Trakia University, Bulgaria
[2]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

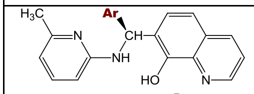
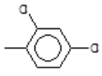
e-mail: nvgeorgieva@vmf.uni-sz.bg

Scientific literature presents data on the high activity of 7-substituted derivatives of 8-hydroxyquinoline against cancer cells in human in combination with cytotoxic activity, activity against HIV etc. The aim of the present study was to synthesize a new 2,4-dichloro-substituted 7-aminobenzyl-8-quinolinol by a modified Betti reaction, to test its microbiological activity against 19 test strains pathogenic microorganisms and to develop analytical methods for its determination.

For modification of the Betti reaction we used 2-amino-6-methylpyridin, 8-quinolinol and 2,4-dichlorobenzaldehyde. The condensation was conducted in absolute ethanol. The reaction mixture was allowed to stand for 21 days at room temperature in a closed flask. The new Betti base was diluted in N,N′-dimethylformamide (concentrations 500 µg/mL), and its microbiological activity was tested against 19 pathogenic microorganisms: *Listeria 215*, *Listeria 362*, *Listeria 1094*, *Staphylococus 1, Staphyloc. 5, Staphyloc. 42, Staphyloc. 78, Staphyloc. 119, Bact. megat 10, Bact. megat 11, Bact. megat 16, Bact. megat 39, Bact. cereus 12, Past. mult. 10, Past. mult. SHp, Past. mult. R II, Salm. Dublin, Salm. Gollinarum 200, E. coli 21*. The compound was also characterized by NMR spectral analyses. Its concentrations in ethanol/HCL (pH 1.0) were measured with UV-VIS spectrophotometer DR 5000 Hach Lange (Germany) at λ 205 nm. RP-HPLC system comprising of a Hypersil BDS C18 (5 µM, 4.6 x 150 mm) column with mobile phase water/methanol (v/v 60:40) (pH 3.2) was used.

The properties of 7-[(6-methylpyridin-2-ylamino)(2.4-dichlorophenyl)methyl]quinolin-8-ol are presented at Table 1. It was established that 7-((6-methylpyridin-2-ylamino)(2,4-dichlorophenyl)methyl)quinolin-8-ol exhibited high microbiological activity inhibiting the growth of 12 of all tested pathogenic bacterial strains. According of the EPR signal, 7-[(6-methylpyridin-2-ylamino)(2,4-dichlorophenyl)methy] quinolin-8-ol possesses radial structure and is likely to exhibit antioxidant activity.

Table 1: Properties of the new Betti base

Betti base	Empirical formula	MG	M.P.,°C	Yd %	%, N Calc.	%, N Found	%, C Calc.	%, C Found	%, H Calc.	%, H Found
 where Ar is 	$C_{22}H_{17}Cl_2N_3O$	410.30	184-186	98	10.24	10.39	64.40	64.22	4.18	3.94

The UV/VIS and HPLC spectra (Fig. 1) of the Betti base characterized with well resolved peaks. The calibration curves of both methods characterized with high regression coefficients (R^2 > 0.996). The UV/VIS method characterized with lower LOD (2.912 µg/mL) and LOQ (8.823 µg/mL) values. Main advantage of the HPLC method is the short detection time - 1.5 min.

In conclusion we assume that the potential of the new Betti bases as a pharmacological compound is great. The applied analytical methods offered short analysis time, high precision, high linearity and satisfactory LOD and LOQ values. Thus, they enhance the capabilities for the accurate and selective determination of the chloro-substituted 7-aminobenzyl-8-quinolinol in low concentrations (1.0 µg/mL) in liquid phase.

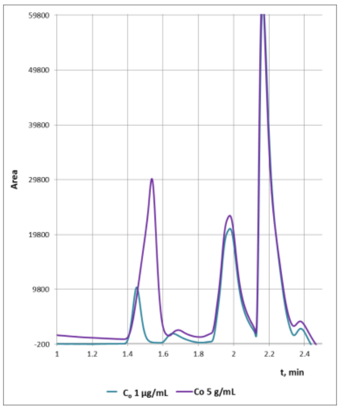


Fig. 1: HPLC spectra of the new Betti base.

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P 15

Solubility of propylene/propane gas in ionic liquids

Tee Yong Goh, Peter Goodrich, David Rooney, Johan Jacquemin

QUILL Research Centre, Queen's University Belfast, Stranmillis Road, BT9 5AG United Kingdom

e-mail: tgoh03@qub.ac.uk

The development of ionic liquids (ILs) has been widely growing in the field of separation science such as olefin and paraffin separation both in gas and liquid phases. A novel approach to separate olefin/paraffin using Task Specific Ionic Liquids has been developed at Queen's University Belfast to not only cut down the production costs but also lower the energy consumption of the operation like gas separation and distillation. In such scheme, the prior knowledge of physical properties such as the gas solubility is essential to select the best solvent. Solvent with good solubility is perfectly matched as medium for gas separations [1]. It is worth pointing out that, there is a variety of experimental methods to determine the olefin/paraffin solubility in ILs. However, new techniques which involve the measurements and predictions of gas solubility of olefin/paraffin in ILs are still essential and thus it is fundamental to be further developed. Thus, the aim of this work was, first, to measure the gas solubility of propane/ propylene in ionic liquids using isochoric and NMR spectroscopy techniques to assess the accuracy of the latter method. Gas solubility has been studied by applying different pressure and temperature to the ionic liquid system. The research concludes that the higher the pressure of olefin/paraffin applied to the IL, the more noticeable the NMR peak of the gas in liquid. The measurement is straightforward and yet effortless. The results obtained in this work have a good agreement with the results reported in the literature and hence proving that the NMR method has a huge potential to be further developed and studied. Also, isochoric saturation system was designed in this work with the purpose to measure the gas solubility of pure and mixed gas of propane/propylene in different ionic liquids. The composition of the gas phases and selectivity of the mixed gas was assessed by a gas chromatography (GC). Finally, COMO-RS method has been used to assess its predictive capability for the prediction of olefin/paraffin solubility in selected ILs. The comparison of the results using both methods will be presented to address their accuracy.

Reference

[1] D. Camper, P. Scovazzo, C. Koval, R. Noble, *Industrial & Engineering Chemistry Research* **43**, 3049-3054 (2004).

P 16

Study of the interaction of Pu, U and Tc with iron corrosion products under highly alkaline conditions

M. R. González-Siso[1], X. Gaona[2], L. Duro[1], D. Schild[2], D. Fellhauer[2], I. Pidchenko[2], T. Vitova[2], M. Altmaier[2], J. Bruno[1]

[1]Amphos 21 Consulting S.L., Passeig Garcia i Faria, 49-51, 1-1a, 08019 Barcelona, Spain
[2]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany

e-mail: maria.rosa.gonzalez.siso@gmail.com

The Swedish Final Repository (SFR1) is used for the final disposal of low- and intermediate-level radioactive waste. Iron will be present in the repository as a structural component in reinforced concrete structure, as main component of steel canisters and as part of the waste materials. The ingress of groundwater in SFR1 repository will impose hyperalkaline and strongly reducing conditions due to its interaction with cement and the anaerobic corrosion of iron. This will have an impact on the chemical behaviour of the redox sensitive radionuclides present in the waste. The determination of the response of the redox sensitive radionuclides to the evolution of the system containing large amounts of iron and concrete is key to the performance assessment of nuclear waste management systems. Redox transitions in the hyperalkaline pH range of for the radionuclides (RN) chosen in this study [Pu(III) $\rightarrow$ Pu(IV) at pH + pe ~ -1; U(IV) $\rightarrow$ U(VI) at pH + pe ~ +2; Tc(IV) $\rightarrow$ Tc(VII) at pH + pe ~ +6] strategically cover the field of stability of the system Fe(0)/Fe(II)/Fe_3O_4, being magnetite the main product of anaerobic steel corrosion.

Separate **s**uspensions of synthetic α-Fe_3O_4(cr) were prepared at solid to liquid ratio (S:L) of 2 $g \cdot L^{-1}$ at 22±2°C under inert gas (Ar) atmosphere ($O_2 < 5$ ppm) at $pH_m \sim 9$ and $pH_m = 12.8$ ($pH_m = -\log m_{H+}$) in 0.1 M NaCl–NaOH solutions. The redox state of the suspensions was controlled by using four different redox systems: a) α-Fe_3O_4(cr) + RN, b) α-Fe_3O_4(cr) + Fe(cr) + RN, c) α-Fe_3O_4(cr) + 0.01 M $SnCl_2$ + RN and d) α-Fe_3O_4(cr) + 0.01 M $Na_2S_2O_4$ + RN. The most soluble redox state of the RN of interest was used in the experiments (Pu(V), U(VI) and Tc(VII)). The initial RN concentration in the resulting suspension was in all cases $3 \cdot 10^{-5}$ M. Samples were equilibrated for up to 260 days; pH_m, redox potential (as pe = $16.9 \cdot E_H$) and [RN] were monitored at regular time intervals. Total radionuclide concentration in solution was quantified by LSC (^{99}Tc and ^{242}Pu) and ICP–MS (^{238}U) after 10 kD ultrafiltration. Plutonium redox speciation in the aqueous phase was investigated by solvent extraction. The redox state of Pu, U, Tc and Fe at the surface of magnetite was characterized by XPS at t = 170 and 260 days. Redox state and molecular environment of Pu in the solid phase was characterized by XANES/EXAFS following the Pu L_{III} edge (18.057 keV) at the INE beamline at ANKA synchrotron facility.

The main results are as follows:

1. The concentration of Pu in solution decreases rapidly to values below or at the detection limit of LSC ($10^{-8.8}$ M) in most of the samples, indicating the reduction of Pu(V) to less mobile redox states. The predominance of Pu(III) in the aqueous phase is thermodynamically predicted in these near-neutral pH and very reducing conditions, and is also confirmed in this study by solvent extraction techniques. XPS confirms the predominance of Pu(IV) on the surface of magnetite, although the presence of Pu(III) is also observed in the most reducing systems ($Na_2S_2O_4$, $SnCl_2$) at $pH_m \sim 9$. Both XPS and XANES analyses confirm the co-existence of Pu(III) and Pu(IV) at $pH_m = 12.8$ for the magnetite system in $SnCl_2$
2. The concentration of uranium decreases below 10^{-8} M in all the samples except those with $pH_m = 12.8$ and less reducing conditions (α-Fe_3O_4(cr) and α-Fe_3O_4(cr) + Fe(cr)), where [U] $\approx 10^{-5}$ M. These observations are in good agreement with the expected formation of $UO_2(OH)_4^{2-}$ under the pe + pH_m conditions defined by both systems.
3. The concentration of technetium in solution decreased steadily from t = 1 day, indicating that Tc(VII) is reduced to Tc(IV) as predicted from thermodynamic standpoint, although the reduction is slower at pe + pH_m values closer to the Tc(VII)/Tc(IV) borderline. The predominance of Tc(IV) on the surface of magnetite is also confirmed by XPS.

Acknowledgements

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P 17

Thermodynamic and phase equilibrium of the solid solution containing system KCl-$RbCl$-H_2O at 298.15 K and 323.15 K

Lijiang Guo, Dongdong Li

Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. 810008 Xining, P. R. China,

e-mail: l.j.guo@hotmail.com

The thermodynamic properties and phase diagram of the solid solution containing system $KCl−RbCl−H_2O$, are of importance both for understanding the losing mechanism of Chaerhan Salt Lake (located in Qaidam Basin, northwest of Chian) rbidium resources in the potash production process, and for extracting Rb from the salt lake. The water activity[1,2] and solubility[2,3,4] for the $KCl−RbCl−H_2O$ system at 298.15 K have been reported. However, up to now, there is no reported water activity and solublity research work at 323.15K. Assuming the equlibriated sollid phases are pure salt(KCl and RbCl), the reported[5] model calculating work on the solubility for this system is unresonable, since the solid phase should be the (K, Rb)Cl solid solution rather than pure salt according to the experiment solubility data[2,3,4].

We measured the water activity for the $KCl−RbCl−H_2O$ system both at 298.15 K and 323.15K by the isopiestic method. The experiment points with a same water activity stand roughly in a straight line, as shown in figure 1, this indicates that the mixing behavior of KCl and RbCl aqueous solution obeys the Zdanovskii's rule. Correlating with the measured water activities, we selected Pitzer model[6] to calculate the solubility of the (K, Rb)Cl solid solution, and then drew the Lippmann diagrams for this solid solution containing system at 298.15 K and 323.15 K.

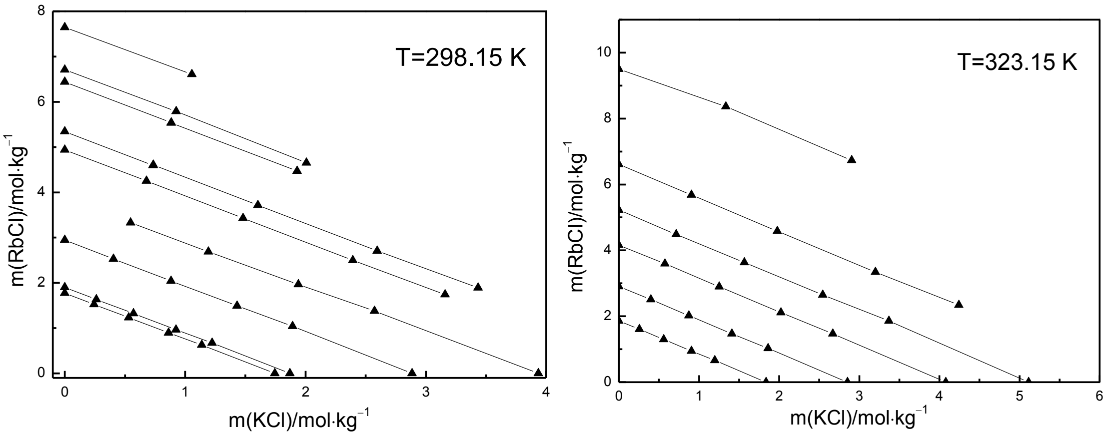

Fig. 1: Measured water activity lines of the $KCl−RbCl−H_2O$ system at 298.15 K and 323.15 K.

References

[1] B. Hu, D.D. Gao, Y. Yao, W. Li. Isopiestic studies on thermodynamic properties for $KCl–RbCl–H_2O$ system at 298.15 K. *Journal of Salt Lake Research* **23**, 45-49 (2015).

[2] A.P. Ratner, L.L. Makarov. A thermodynamic study of the system $KCl–RbCl–H_2O$ at 25 Degrees C. *Zhurnal fizicheskoi Khimii* **32**, 1809-1816 (1958).

[3] A. Merbach, J. Gonella. Contribution à l'étude du système quaternaire $KCl–RbCl–CsCl–H_2O$: I. Les isothermes de 25° des systèmes ternaires limites. *Helvetica Chimica Acta* **52**, 69-76 (1969).

[4] J. D'Ans, F. Busce. On fractioning of incongruently soluble isomorphic double salts-The quaternary systems $KCl–RbCl–(CsCl)–MgCl_2–H_2O$ at 25 °C. *Zeitschrift für Anorganische und Allgemeine Chemie* **232**, 337-368 (1937).

[5] C. Christov, S. Petrenko, C. Balarew, V. Valyashko. Thermodynamic simulation of four-component carnallite type systems. *Monatshefte für Chemie* **125**, 1371-1382 (1994).

[6] K.S. Pitzer. Thermodytriarnics of electrolytes. I. theoretical aasis and general equations. *J. Phys. Chem. 77*, 268-277 (1973).

P 18

A class of efficient short-chain fluorinated catanionic surfactants

Tee Yong Goh, Johan Jacquemin, Pedro Verdia, H.Q. Nimal Gunaratne, Pia McAleenan, Marijana Blesic

Queen’s University Belfast, Stranmillis Road, BT9 5AG United Kingdom

e-mail: m.blesic@qub.ac.uk

In this work, synthesis and physico-chemical properties of a series of catanionic fluorinated surfactants are presented. The surfactants are characterised with excellent fluorine efficiency and surface tension reduction. They also show good water solubility, low Krafft points and potentially better degradation, A novel molecular design demonstrated in this work offers the most efficient way to achieve very low limiting surface tension in an aqueous solution approaching the surface tension of neat fluorocarbons, at the same time keeping the fluorine efficiency high. A very low surface tension that has been reported in this study could lead to an extension of application of surfactants in different fields that have not yet been explored.

P 19

New method for the estimation of viscosity of pure and mixtures of ionic liquids based on the UNIFAC-VISCO model

Nan Zhao[1], Ryan Oozeerally[2], Volkan Degirmenci[2], Zdeněk Wagner[3], Magdalena Bendová[3], Johan Jacquemin[1]

[1] School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK
[2] School of Engineering, University of Warwick, Coventry CV4 7AL, UK
[3]E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals AS CR, v. v. i. Rozvojová 135, 165 02 Prague 6 – Suchdol, Czech Republic

e-mail: johan.jacquemin@qub.ac.uk

A modified UNIFAC-VISCO group contribution method was developed for the correlation and estimation of viscosity of ionic liquids as a function of temperature at 0.1 MPa using a large set of recommended data from the literature. During this work, experimental data were critically assessed using the statistical method and mathematical gnostics to highlight recommended data used then to develop the modified UNIFAC-VISCO model. In this original approach, the ionic liquid was divided into two peculiar function groups, cation and anion. Binary interaction parameters were determined by fitting the experimental viscosity and by minimizing the objective function. The viscosity of cations, anions, and ILs showed an exponential behavior with the temperature well described thanks to the Vogel-Fulcher-Tamman (VFT) equation. Calculated VFT constants and binary interaction parameters were used to predict the viscosity of pure and mixtures of ionic liquids. The estimation result showed a good agreement with experimental data with a relative absolute average deviation lower than 1.7 %. This novel approach will be presented and discussed in detail during our presentation.

Keywords: Ionic Liquids, UNIFAC-VISCO, Viscosity, Estimation, Temperature

P 20

Solubility and complex formation of zirconium carbonate in dilute to concentrated $NaNO_3$

Taishi Kobayashi, Takayuki Sasaki

Department of Nuclear Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku 615-8540, Kyoto, Japan

e-mail: kobayashi@nucleng.kyoto-u.ac.jp

For the safety assessment of radioactive waste disposal, it is necessary to predict radionuclide solubility limits under relevant disposal conditions. Actinide elements such as uranium, neptunium and plutonium in the radioactive waste have long half-life and the solubilities are primarily controlled by sparingly soluble hydroxides of tetravalent actinides ($An(IV)(OH)_4$(am)). In spite of the strong hydrolysis reaction, the complex formation of An(IV) with carbonate is one of the most important reactions for the reliable prediction of the An(IV) solubility. Since part of low-level wastes (TRU waste) generated from Japanese nuclear reprocessing process contain considerable amount of nitrate salt, an impact of dilute to concentrated $NaNO_3$ on the complex formation of An(IV) carbonate need to be clarified within the context of co-disposal of TRU waste and high level waste. Although a comprehensive literature review has been performed on the thermodynamic constant of actinide including the An(IV) carbonate [1], the literature data on An(IV) carbonate at high ionic strength is still lacking. In the present study, we focus on the complex formation of Zr(IV) carbonate, which is known as an analogue of An(IV). Zirconium is also a relevant element in the safety assessment of radioactive waste disposal, since it has a high yield among the uranium fission products and zirconium metal is used as a fuel-cladding in light water reactors. However, limited thermodynamic data on Zr carbonate at low to high ionic strength is available [2]. Zr solubility in carbonate solution containing 0.1 to 5.0 mol/dm^3 (M) $NaNO_3$ was measured and discussed based on the thermodynamic constant and existing activity correction model.

Amorphous zirconium hydroxide solid phase ($Zr(OH)_4$(am)) was pre-precipitated and washed with purified water several times. The $Zr(OH)_4$(am) was then added into the solutions at certain pH, total carbonate concentration ($[C]_{tot}$), and ionic strength (I). The pH was adjusted in the range of pH 7 - 12 by HNO_3/NaOH and the ionic strength was controlled to be 0.1, 0.5, 2.0 and 5.0 M by $NaNO_3$. The $[C]_{tot}$ was adjusted to be 0.015 - 0.1 M by $NaHCO_3$. After given aging time, the supernatant of the sample solution was filtrated though ultrafiltration membranes (10 kDa NMWL) and Zr concentration was determined by ICP-MS.

The solubility in 0.04 M $[C]_{tot}$ at $I = 0.1$ was 10^{-4} M in the neutral pH region and decreased with pH at pH > 9. The solubility was near 10^{-8} M at pH > 11. The solubility at the same $[C]_{tot}$ slightly increased with increasing I and that in the neutral pH region at $I = 5.0$ was about 10^{-3} M. From the results of slope analysis of the Zr solubility, dominant soluble species were considered to be $Zr(CO_3)_4^{4-}$ and $Zr(OH)_2(CO_3)_2^{2-}$. The complex formation constants and ion interaction coefficients were determined from the solubility data based on the SIT approach.

References

[1] R. Guillaumont *et al.*, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. Elsevier, Amsterdam, 2003.
[2] P. Brown *et al.*, *Chemical Thermodynamics of Zirconium*. Elsevier, Amsterdam, 2005.

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P 21

Solid-aqueous equilibrium in the Na, K, Rb, Mg // Cl − H_2O system: Experiments, *ab initio* and thermodynamic modelling

Dandan Gao[1], Dongdong Li[1], Ronggang Huang[2], Wu Li[1], Dewen Zeng[3]

[1]Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, P. R. China
[2]College of Chemical Engineering, Qinghai University, Xining 810006, P. R. China
[3]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China

e-mail: ddong_li@hotmail.com

Rubidium is important addition agent in many high-tech applications. Rubidium salts can be obtained as valuable by-products in potash production. Salt lake brines and natural carnallite are the most common raw materials for potash production [1]. The behavior of rubidium during the evaporation of brine and decomposition of carnallite is of great significance to reveal how rubidium can be concentrated. Understanding the partition of rubidium between solid and aqueous phase in potash production requires the phase equilibria information of the Na, K, Rb, Mg // Cl − H_2O system for a broad temperature range. In this study, a temperature dependent thermodynamic model for the Na, K, Rb, Mg // Cl − H_2O system is developed within the Pitzer-Simonson-Clegg (PSC) framework [2,3] based on the available thermodynamic and phase equilibria data in literature, new data of RbCl + H_2O and NaCl + RbCl + H_2O systems determined in our group, and regular solution parameters for sylvite and carnallite solid solutions estimated from atomic simulations technology introduced by Vinograd *et al.* [4,5]. To verify the reliability of the present model, phase diagrams of the system KCl + RbCl + $MgCl_2$ + H_2O at various temperatures collected from literature and phase diagram of the system NaCl + KCl + RbCl + H_2O at 298.15 K experimentally determined by us are compared with the model predictions. Furthermore, the partition behavior of rubidium between phases is simulated for real brines evaporation and freezing processes.

References

[1] R. Ratner, J. Mittelman, D.H. Kohn, *J. Chem. Tech. Biotechnol.* **35A**, 209 (1985).
[2] S.L. Clegg, K.S. Pitzer, P. Brimblecombe, *J. Phys. Chem.* **96**, 9470 (1992).
[3] D. Li, D. Zeng, H. Han, L. Guo, X. Yin, Y. Yao, *Calphad* 511 (2015).
[4] V.L. Vinograd, B. Winkler, *Rev. Mineral. Geochem.* **71**, 413 (2010).
[5] V.L. Vinograd, F. Brandt, K. Rozov, M. Klinkenberg, K. Refson, B. Winker, D. Bosbach, *Geochim. Cosmochim. Acta* **122**, 398 (2013).

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P 22

Accurate measurement of the co-saturation lines in the NaCl-$MgCl_2$-H_2O system and its application for $MgCl_2·6H_2O$ purification using re-crystallization method

Haijun Han[1,2,3], Ouyang Dong[2], Dongdong Li[2], Dewen Zeng[3]

[1]School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, P.R. China
[2]Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, P.R. China
[3]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P.R. China

e-mail: ddong_li@hotmail.com

The present work was initiated by a strange phenomenon we have met, that is, the impurity NaCl in the main product $MgCl_2·6H_2O$ is easy to remove by conventional re-crystallization approach when the NaCl content is low, however, hard to remove at high NaCl content. To understand the essence of the strange phenomenon and to search for an effective separation approach by re-crystallization, the co-saturation line for the solid phases $NaCl_{(s)}$ and $MgCl_2·6H_2O_{(s)}$ in aqueous solution has been elaborately measured by a phase equilibrium method at various temperatures. It was found that the Y_b ($Y_b=w(NaCl)/(w(NaCl)+w(MgCl_2))$) value of the co-saturation line increase with increasing temperature, ending the confusing state of the data concerning the co-saturation line from literature. Combining the new obtained results and general phase rules, one can profoundly understand the essence behind the strange phenomenon. A new recrystallization approach has been suggested for the purification of $MgCl_2·6H_2O_{(s)}$ containing quite amount of impurity NaCl, i.e., dissolving the crude sample at low temperatures, followed by evaporating and phase separating at high temperatures. Applying the proposed approach a crude $MgCl_2·6H_2O_{(s)}$ sample with Y_b=1.21% can be purified to the level of Y_b=0.17% by only one crystallization process.

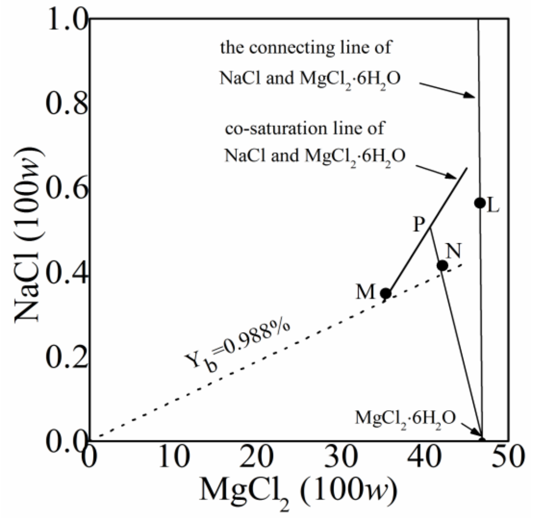

Fig. 1: Purification process of the $MgCl_2·6H_2O_{(s)}$ sample with Y_b=1.21%.

References

[1] D. Li, D. Zeng, *et al.*, *Journal of Salt Lake Research* **21**, 32-37 (2013).
[2] W.F. Linke, A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds,* fourth ed.; American Chemical Society: Washington DC, 1965.

P 23

A new method for the measurement of fugacity and the Henry's law constant for volatile organic compounds containing chromophores

Keith B. Lodge

University of Minnesota Duluth, Chemical Engineering, 1303 Ordean Court, Duluth, Minnesota 55812-3025, U.S.A.

e-mail: klodge@d.umn.edu

In this poster, a summary of the important background paper[1] to an author's talk[2] at ISSP17 will be presented.

A new method for the measurement of the fugacity and the Henry's law constant for volatile organic compounds containing chromophores is described; this was tested with benzene, toluene and ethylbenzene distributed between air and water. The steadily flowing vapor phase of fixed composition is prepared with a mass-flow controller and syringe pump – a method that has been used to calibrate the adsorption by fibres in solid-phase micro extraction. The vapor phase flows in and out of the head space above pure water in a 1-cm spectrophotometric cell – housed in a temperature-controlled holder in a UV-Visible spectrophotometer. The approach to equilibrium – as the chemical is transferred from the vapor to the stirred liquid phase – is monitored by following the absorbance of the liquid phase at a selected wavelength. Calibration leads to the following molar absorption coefficients (± standard errors, units of L mol^{-1} cm^{-1}) in water at 25 °C; for benzene at 260 nm, 101 ± 1; for toluene at 261 nm, 284 ± 1; and, for ethylbenzene at 257 nm, 253 ± 3. The fugacities are linear with respect to the mole fractions in the water. The resulting Henry's law constants (± standard errors, units of 10^4 kPa) are comparable to published values; at 25 °C, these are for benzene, 2.22 ± 0.05; for toluene, 3.99 ± 0.04; and for ethylbenzene, 5.14 ± 0.06.

References

[1] K.B. Lodge, D. Danso, *Fluid Phase Equilibria* **253**, 74-79 (2007).

[2] K.B. Lodge, "The prediction of equilibrium and the studies of the rate of mass transfer of the solute, toluene, to and from a head space with constant composition to a stirred aqueous phase in a spectrophotometric cell", *OC 38,* Friday morning, July 29th.

P 24

Thermodynamics (solubility and protonation constants) of risedronic acid in different media and temperatures (283.15 K to 318.15 K)

Clemente Bretti[1], Concetta De Stefano[1], Gabriele Lando[1], Kavosh Majlesi[2],
Silvio Sammartano[1]

[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy
[2]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

e-mail: kavoshmajlesi@srbiau.ac.ir

Risedronic acid (1-hydroxy-1-phosphono-2-pyridin-3-yl-ethyl phosphonic acid) belongs to the class of ligands called Bisphosphonates (BPs), which are the most important drugs used to treat bone-resorption diseases. The mechanism of action consists in the inhibition of the enzyme farnesyl diphosphate synthase, preventing osteoclastic bone resorption. Risedronic acid is generally indicated for the prevention or treatment of postmenopausal and glucocorticoid-induced osteoporosis and Paget's disease. In the last decades there is a great interest for the development of methods to understand the nature of the bisphosphonate–bone mineral recognition and binding mechanisms, therefore thermodynamic data are necessary to enable the prediction of important technological and pharmacological equilibria.

In this contribution potentiometric measurements were carried out to study the protonation constants of risedronic acid in $NaCl_{(aq)}$, $(CH_3)_4NCl_{(aq)}$ and $(C_2H_5)_4NI_{(aq)}$ at different ionic strengths and temperatures ($283.15 \leq T$ / K ≤ 318.15). In the same conditions, solubility measurements were also performed. Calorimetric measurements were done to determine the protonation enthalpy values at different ionic strengths and 298.15 K.

It was found that the protonation constants in $NaCl_{(aq)}$ are lower than in the two tetraalkylammonium salts, and the medium effect was interpreted using different thermodynamic models [Debye-Hückel type and SIT (Specific ion Interaction Theory)], in terms of variation of the activity coefficients with ionic strength or formation of weak complexes between risedronate and the ions of the supporting electrolytes. The total solubility of risedronate is higher in $NaCl_{(aq)}$ than the other two ionic media and, in all cases, increases with increasing temperature. Setschenow coefficients of neutral species were also computed in all the ionic media. Generally, the proton binding process resulted endothermic and the driving force is entropic in nature. Finally, data in this work were critically compared with literature findings [1].

Keywords: Risedronic acid, Protonation constant, Solubility

References

[1] C. Bretti, I. Cukrowski, C. De Stefano, G. Lando, *J. Chem. Eng. Data* **59**, 3728-3740 (2014).

P 25

CO_2 chemisorption in acetate ionic liquids and ethylene glycol mixtures

Takashi Makino[1], Tatsuya Umecky[2], Mitsuhiro Kanakubo[1]

[1] Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Japan
[2]Graduate School of Science and Engineering, Saga University, Japan

e-mail: makino.t@aist.go.jp

CO_2 separation is an important technology for chemical industry, like the flue gas treatment, the production of energy resources like hydrogen and methane, and so on. Absorption is the most general-purpose method, and a variety of absorbents have been developed. Amine aqueous solutions are well-studied chemical absorbents, in which CO_2 is absorbed through chemical reactions. However, the amine solutions have some critical issues, i.e. the high energy consumption for CO_2 desorption and the loss and flammability of absorbents. Ionic liquids (ILs) have drawn much attention as a possible chemical absorbent, which can overcome the issues of amine aqueous solutions. ILs are salts with the melting points at or below ambient temperature. They have some favorable characteristics as CO_2 absorbent: non-volatility, non-flammability, low heat capacity, and high solubility of CO_2. On the other hand, ILs are rather viscous than conventional amine aqueous solutions. Some earlier studies proposed the mixed absorbents of ILs and organic solvents for the viscosity reduction. In the present study, we investigated the CO_2 chemical absorption in the mixtures of acetate based ILs and ethylene glycol. It is well known that some acetate salts absorb CO_2 chemically, and their production costs are less expensive than other chemical IL absorbents. In addition, our recent study revealed that the introduction of the hydroxyl group in the acetate ILs strongly influences the CO_2 chemisorption. In the present study, we measured the CO_2 solubility at atmospheric pressure in the ethylene glycol solutions of 1-ethyl-3-methylimidazolium acetate ([emim][AcO]) and *N*,*N*-diethyl-*N*-heptyl-*N*-methylammonium acetate ([N_{1227}][AcO]) over the temperature range from 283 K to 373 K. The addition of ethylene glycol diminished the CO_2 solubility in [emim][AcO], whereas it enhanced the solubility in [N_{1227}][AcO]. The 67 mol% [N_{1227}][AcO]-ethylene glyol mixture absorbed the larger amount of CO_2 than the 50 mol% [N_{1227}][AcO] mixture. The ^{13}C NMR spectra indicated the formation of the ethylene glycol-CO_2 complex in the [N_{1227}][AcO] mixtures, and the ethylene glycol-CO_2 as well as carbene-CO_2 complexes in the [emim][AcO] mixtures.

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P 26

Unicellular planktonic organisms: an intracellular environment chemically different from the surrounding freshwater

Agathe Martignier[1], Montserrat Filella[1], Jean-Michel Jaquet[1], Pascale Nirel[2], Daniel Ariztegui[1]

[1]Section des Sciences de la Terre et de l'environnement, Université de Genève, Switzerland
[2]Service de l'Ecologie de l'Eau, DIME, Genève 8, Switzerland

e-mail: agathe.martignier@unige.ch

Mineral intracellular inclusions have recently been discovered in widespread unicellular planktonic organisms. These micron-scale amorphous carbonate inclusions, showing internal concentric layers, are called micropearls. The organisms forming them live in strongly under-saturated waters (e.g. Lake Geneva). The formation of micropearls rich in Sr and Ba in such conditions can only be explained by a drastically different chemical environment inside the cell, strongly enriched in Ba, Sr and Ca. Our current research aims to better understand the formation of these micropearls and to establish to what extent their composition is influenced by the composition of the surrounding freshwater.

P 27

Dissolution of intermediate grade phosphate by a dilute mixture of phosphoric acid and sulfuric acid. Influence of certain parameters

Abbes Mizane[1], Salah Belhait[2]

[1]Laboratory of Water Treatment and Recycling of Industrial Waste, Department of Chemistry, University Badji Mokhtar, BP12, 23000, Annaba, Algeria
[2]Department of Chemistry, University Badji Mokhtar, Annaba, Algeria

e-mail: abbes.mizane@univ-annaba.dz

In this study, the first part concerns the study of the influence of certain parameters on the dissolution of phosphate rock 53.75% BPL (bone phosphate of lime) by a mixture of phosphoric acid and sulfuric acid. PAPRs (Partially Acidulated Phosphate Rocks) is obtained by performing a series of reactions using a mixture of phosphoric acid and sulfuric acid having low concentrations (10 to 40 wt %). Experiments performed with phosphate at different particle size (88 -500 µm) show that the P_2O_5 recovery increases with increasing sulfuric acid -phosphoric acid ratio but it is inversely proportional to the phosphate particle size.

In the second part, experiments showed that the water-soluble P_2O_5 has reached 17.4% for PAPRs obtained by reacting phosphate 88 µm with a mixture of H_3PO_4 30 wt. % and H_2SO_4 40 wt. %. It has been established in this study that he addition of sulfuric acid enhances the dissolution of phosphate rock by phosphoric acid. Therefore, the production of PAPRs may be feasible with intermediate-grade phosphate and modest levels of acids concentration.

Keywords: PAPRs, phosphate rocks, mixture phosphoric sulfuric acid, water-soluble P_2O_5

P 28

Modelling of REE carbonate precipitation in sulphate rich solutions

Risto Pajarre

Aalto University, School of Chemical Technology, Dept of Materials Science and Engineering, P.O. Box 1620,
FI-00076 Aalto, Finland

e-mail: risto.pajarre@vtt.fi

A Pitzer interaction based model has been applied to REE separation from a sulphate solution by carbonate precipitation. The initial model that lacked parameters for the interactions between the REE and sulphate ions was noted to clearly and systematically underestimate the carbonate precipitation. Without ion specific interaction parameters the activity coefficients obtained from Pitzer formalism are very low for multivalent ions in solution of high ionic strength, even if the multivalent ion itself is not present in high concentrations. Model with interaction parameters adopted from Fe(III)-SO4 sulphate system gave reasonable match with both laboratory experiments and pilot scale plant results.

Implications for practical application of Pitzer electrolyte models for systems with limited data is discussed together with the need and possibilities to apply estimated interaction parameters with multivalent ions.

P 29

Hydrometallurgical treatment of jarosite waste

Petteri Kangas[1], Risto Pajarre[1], Inka Orko[1], Mari Lundström[2], Pertti Koukkari[2,1]

[1]Aalto University, School of Chemical Technology, Dept of Materials Science and Engineering, P.O. Box 16200,
FI-00076 Aalto, Finland
[2]VTT – Technical Research Centre of Finland, FI02044-VTT, Finland

e-mail: risto.pajarre@vtt.fi

Jarosite is a leach residue produced by industrial bulk metal treatment processes and typically has the chemical formula $M_xFe_3(SO_4)_2(OH)_6$, where M represents a metal cation. The largest source of jarosite is electrolytic zinc processing [1], which worldwide has an annual production of 11-12 Mt Zn with adjacent 5-6 Mt jarosite or goethite, normally classified as problem waste. The precipitation of jarosite will equally bind the minority metals present in the aqueous electrolyte solution into the M position. Thus, e.g. gallium is readily precipitated in jarosite-type compounds and the extent of gallium bound in jarosite increases as the Ga concentration of the solution increases. Similar precipitation behaviour is encountered with indium and thus these two critical metals are also often present in significant amounts in jarosite heaps. An analysis of jarosite from Kokkola, Finland found that it contained as much metal as many present day commercial ores: ~15% iron, 2% zinc, 3 % lead, 150 g/t silver, 0.5 g/t gold, 100 g/t indium and 40 g/t gallium. Jarosite related research has concentrated on its use in landfill and construction purposes [2], though there is increasing interest in finding methods to efficiently reprocess/recycle jarosite into valuable products [3, 4]. The hydrometallurgical process currently under development by VTT and Aalto University exploits jarosite's powdery nature and varied cationic solubility to undertake wet chemical processing. This low cost and energy efficient operation is targeted at the recovery of concentrates which contain the major value-added metals.

References

[1] E. Moors, G. Dijkema, Embedded industrial production systems - Lessons from waste management in zinc production. *Technol. Forecasting & Social Change* **73**, 250-265 (2006).
[2] E.N. Rathore, M.P. Patil, E. Devendra Dohare, Utilisation of jarosite generated from lead-zinc smelter for various applications. *Int. J. Civil Eng. & Technol.* **5**, 192-200 (2014).
[3] United Nations Environment Programme, (2013), Metals Recycling Full Report.
[4] J. Rastas, A. Jarvinen, V. Hintikka, J. Leppinen, Recovery of lead, silver and gold in the zinc process and possibility of non-waste technology in zinc production. VTT Symposium (1989), 103 (Non-Waste Technol., Vol. 2), 235-51.

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Water solubility of terpenes and terpenoids

Mónia A.R. Martins[1], Liliana P. Silva[1,2], Olga Ferreira[2], Bernd Schröder[1], Simão P. Pinho[2], João A.P. Coutinho[1]

[1]CICECO, Departamento de Química, Universidade de Aveiro, Portugal
[2]Associate Laboratory LSRE-LCM, Instituto Politécnico de Bragança, Portugal

e-mail: spinho@ipb.pt

Terpenes and terpenoids belong to what is probably the largest and most diverse class of natural products and the vast majority are found only in plants. They are components of essential oils, flavours, spices and fragrances. With the increasing importance of their practical applications in the fragrance and flavour industries, as well as in the pharmaceutical and chemical industries, process-relevant physico-chemical data of terpenes and terpenoids have been retrieved over time. Meanwhile, with an emerging perception of terpenes and terpenoids impact on the environment, right through to implications on a global scale, those data are proving to be insufficient.

In this work, we report the water solubility of carvacrol, thymol, eugenol, geraniol, linalool, DL-citronellol, (1R)-(−)-Fenchone, (1R)-(+)-camphor, eucalyptol, (R)-(+)-limonene, (S)-(+)-carvone, (−)-menthone, and (−)-isopulegol, in the temperature range from (298.15 to 323.15) K. Due to the very low solubility values, a special approach has been followed for the solubility measurements; a saturated aqueous solution was generated within a dialysis tubing, followed by careful sampling and dilution in methanol. The process was speeded up using an ultrasonic bath with temperature control before the equilibrium step. The main advantage of the present technique is to avoid sampling of solute not dissolved, but present in micro-emulsions, a common experimental error, which often leads to overestimated solubility values. UV spectroscopy was used for quantitative analysis.

Results show that the applied experimental method provides accurate aqueous solubility data for these sparingly soluble compounds.

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Indium and gallium whole-genome phenotypic screening in yeast and culture media speciation modelling

Yves Schulze[1], Montserrat Filella[1], Payam Ghiaci[2], Jonas Warringer[2], Markus J. Tamás[2]

[1]Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland
[2]Dept. of Chemistry and Molecular Biology, University of Gothenburg, Lundberg Laboratory, Box 462
Medicinaregatan 9C, 405 30 Göteborg, Sweden

e-mail: yves.schulze@etu.unige.ch

The field of functional genomics is currently developing automated whole-genome phenotypic screening approaches to measure the growth rates of single gene knockout yeasts. Yeast is one of the best characterized eukaryotic model organisms because of its fast replication time, cheapness in comparison to more evolved organisms and the effective high-throughput tools that were developed by the scientific community [1]. Yeast can be used as a tool to improve our understanding of conserved biological mechanisms that relate environmental toxicants to human health [2]. One of the major challenges is the complexity of the culture medium that is used and the difficulty to understand the speciation of the toxicants that are introduced. We are currently undertaking genome-wide phenotypic screenings to identify the genetic bases for indium and gallium sensitivity/tolerance in yeast using a novel framework for high-resolution phenomics on solid media [3]. Our work is affiliated to the European COST action TD1407 that on the behalf of the European Commission defines Indium and Gallium as critical metals necessary for future technological and economic developments but at risk to become increasing pollutants [4]. To take into account the speciation of indium and gallium in our culture medium, we aim to take advantage of the thermodynamic data that is available in scientific literature. We are building a consistent computational database with the JESS (Joint expert speciation system) software that should contain all the existing thermodynamic constants that are available [5] for these elements in aquatic media. The database will be made accessible to a wide range of scientists. We hope that it will help us to design experiments with a medium where we can better characterize the behavior of metals and their toxicity.

References

[1] G. Giaever, C. Nislow. The yeast deletion collection: A decade of functional genomics. *Genetics* **197**, 451-465 (2014).
[2] S. C. Dos Santos, M. Cacho Teixeira, T.R. Cabrito, I. Sá-Correia, Yeast toxicogenomics: genome-wide responses to chemical stresses with impact in environmental health, pharmacology, and biotechnology. *Frontiers in Genetics* **3** (April 19, 2012). doi:10.3389/fgene.2012.00063.
[3] M. Zackrisson, J. Hallin, L.-G. Ottosson, P. Dahl, E. Fernandez-Parada, E. Ländström, L. Fernandez-Ricaud *et al.*, Scan-O-Matic: High-resolution microbial phenomics at a massive scale. *bioRxiv* (November 12, 2015) 31443. doi:10.1101/031443.
[4] A. Cobelo-García, M. Filella, P. Croot, C. Frazzoli, G. Du Laing, N. Ospina-Alvarez, S. Rauch, P. Salaun, and J. Schäfer, COST Action TD1407: Network on Technology-Critical Elements (NOTICE)-from environmental processes to human health threats. *Environmental Science and Pollution Research International* **22**, 15188 (2015).
[4] P.M. May, K. Murray, Database of chemical reactions designed to achieve thermodynamic consistency automatically. *Journal of Chemical & Engineering Data* **46**, 1035-1040 (2001).

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Determination of solubility-controlling phases in chromium ore processing residue

Amritanshu Shriwastav, Mainak Bhattacharya, Abhas Singh

Department of Civil Engineering, Indian Institute of Technology, Kanpur, U. P., India

e-mail: abhas@iitk.ac.in

Leaching of toxic hexavalent chromium [Cr(VI)] from unregulated industrial dumpsites of chromium ore processing residue (COPR) is a serious environmental concern in the leather-manufacturing centres of India and the developing world that still use the “high lime” process. The leachates from these sites affect quality of municipal water supplies or groundwater. COPR is a mixture of several crystalline phases that act as hosts for chromium. Yet, the most labile and dominant phases that control the leaching of Cr(VI) under approximate *in situ* conditions are not well understood. Through a series of equilibrations with synthetic rainwater, groundwater and $CaCl_2$ in batch and flow-through reactor experiments, the solubility-controlling phase(s) in COPR were identified and their leaching behaviour modelled. The products of leaching – dissolved Cr(VI), dissolved Cr(III) and secondary Cr and non-Cr phases were identified through IC-ICP MS, SEM and XRD characterizations. Results were interpreted using a carefully selected thermodynamic database relevant to chromium speciation. Findings from this study will likely benefit remediation of Cr-contaminated groundwater.

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Solution–solid equilibria in ternary systems CdI_2 – $Solv_1$ – $Solv_2$ ($Solv_{1,2}$ – DMSO, 1,4-dioxane, DMA, DMF, water)

Olga S. Pushikhina, Nikita A. Bogachev, Mikhail Yu. Skripkin

Saint-Petersburg State University, Saint-Peterburg, Russia

e-mail: n.bogachev@spbu.ru

The development of an integrated physicochemical way to describe the processes occurring in electrolyte solutions and heterogeneous systems is the key point for the prediction of the macroscopic properties of solutions, as well as to create the new universal methods of synthesis of compounds in liquid phase. The research relevance is determined by the lack of a common framework for the fundamental theory of solutions and a detailed model of such processes as dissolution, crystallization and solvation. The absence of the general theory makes quite actual the study of some particular problems among which solubility problem plays one of the key roles.

In this report the results of the study of solid-solution equilibrium in the ternary aqua-organic and mixed organic systems containing oxygen donating aprotic organic solvents with widely different properties like DMSO, DMA, DMF, and 1,4-dioxane, as well as cadmium iodide are presented.

As we have mentioned before [1], in the systems CdI_2-Solv-H_2O (Solv = DMSO, DMA or DMF) at 25 °C three different crystallosolvates are formed depending on binary solvent composition: $CdI_2\cdot$(Solv), $CdI_2\cdot$2(Solv) and $CdI_2\cdot$3(Solv). The first and the second forms are coordination polymer and dimer respectively, whereas the third one is an ionic pair consisted from octahedral cation $[Cd(Solv)_6]^{2+}$and tetrahedral anion $[CdI_4]^{2-}$. The substitution of water by second organic solvent in ternary systems can result in the expansion of the number of solids that is potential to obtain. But preferational solvation phenomena in solutions leads to formation of limited number of compositions.

In this work we are going to demonstrate the effect of solvent composition on solubility of cadmium iodide, composition of crystallosolvates and extensions of their crystallization fields. The results will be explained in framework of Hard and Soft Acids and Bases theory in Marcus quantity approach [2], and also by donor-acceptor interactions [3, 4].

References

[1] N.A. Bogachev *et al., Russian Journal of General Chemistry* **86**, (2016), in press.
[2] Y. Marcus, *The Journal of Physical Chemistry* **91**, 4422-4428 (1987).
[3] V. Gutmann, *Coord. Chem. Rev.* **18**, 225 (1976).
[4] U. Mayer *et al., Monatshefte für Chemie* **106**, 1235 (1975).

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The super enrichment in Sr and Ba of micropearls in Lake Geneva

Bruno Thien[1,2], Agathe Martignier[3], Jean-Michel Jaquet[3], Montserrat Filella[4]

[1]Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen, Switzerland
[2]Fluid and Minerals Resources Group, ETH, 8092 Zürich, Switzerland
[3]Department of Earth Sciences, University of Geneva, 1205 Geneva, Switzerland
[4]Institute F.-A. Forel, University of Geneva, 1205 Geneva, Switzerland

e-mail: bruno.thien@psi.ch

The presence in phytoplankters of intracellular inclusions of amorphous strontium- and barium-rich calcium carbonates –named micropearls– has been recently observed in Lake Geneva [1]. It was measured that those micropearls are several orders of magnitude more enriched than lake water in Sr and Ba. We found that it could be explained by an enrichment in Sr and Ba of the water inside the cells (via carboxylate-like groups), combined with the growth uptake kinetic effect [2]. The application of a growth uptake kinetic model, which describes the growth rate dependency of Sr and Ba in carbonates, allows to estimate the time scale of formation of the micropearls.

References

[1] A. Martignier *et al.*, Intracellular amorphous carbonates uncover a new biomineralization process in eukaryotes. (2016) Under review.
[2] B.M.J. Thien, D.A. Kulik, E. Curti, A unified approach to model uptake kinetics of trace elements in complex aqueous - solid solution systems. *Applied Geochemistry* **41**, 135-150 (2014).

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Solubility of tetravalent UO_2(am,hyd) in alkaline carbonate solutions

Ezgi Yalcintas, Xavier Gaona, Marcus Altmaier

Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany

e-mail: ezgi.yalcintas@kit.edu

An accurate knowledge of the aquatic chemistry and thermodynamics of actinides is fundamental in the context of nuclear waste disposal. The availability of complete and correct chemical and thermodynamic models represents a key milestone in the development of reliable geochemical model calculations and source-term estimations and, thus, in the safety assessment of repositories for nuclear waste disposal. Uranium contributes with the largest inventory to the radioactive waste. U(VI) is the most stable oxidation state of uranium under anoxic and oxidising conditions, whereas U(IV) prevails in strongly reducing environments, forming the sparingly soluble UO_2(am,hyd) ([U] $< 10^{-8}$ M) in solutions with pH ≥ 5 and in the absence of complexing ligands. The predominance of the latter oxidation state is expected in deep geological repositories, where very reducing conditions are foreseen due to the anoxic corrosion of steel. Carbonate has a special relevance in the long-term performance assessment of nuclear waste repositories due to its abundance in ground waters and strong complexation properties with “hard” Lewis acids such as actinides. Previous studies available in the literature have shown that the formation of An(IV) complexes with carbonate significantly increases the solubility of the otherwise sparingly soluble AnO_2(am,hyd), and thus can play an important role in the migration of actinides from the repository to the biosphere [1-3]. In spite of the relevance of uranium in the context of nuclear waste disposal, systematic solubility and thermodynamic studies with U(IV) as a function of carbonate concentration, ionic strength and pH are so far lacking. Based on a combination of comprehensive solubility experiments and accurate solid phase characterization, this work aims at developing complete and correct chemical, thermodynamic and activity models for U(IV) in alkaline carbonate solutions.

Solubility experiments on the U(IV)-carbonate system were performed from undersaturation conditions at $T = 22 \pm 2$°C in Ar gloveboxes with < 2 ppm O_2. A 0.1 M U(IV) solution was prepared by electrochemical reduction of a U(VI) stock solution in 1.0 M HCl and $E \approx -100$ mV *vs. SHE*. Reduction was followed by the quantitative precipitation of U(IV) in 10 mM $Na_2S_2O_4$ solution at $pH_m > 12$. The resulting UO_2(am,hyd) was aged in the mother solution liquors at room T for three months before further use. A first series of experiments was conducted in solutions with total carbonate concentrations of $C_{tot} = [HCO_3^-] + [CO_3^{2-}] = 0.1$, 0.04 and 0.015 M at constant ionic strength $I = 0.5$ M $NaHCO_3$–Na_2CO_3–NaCl. A second series of experiments was prepared with $C_{tot} = 0.02$ M at different ionic strengths, $I = 0.1$, 0.5, 2.0 and 4.0 M $NaHCO_3$–Na_2CO_3–NaCl. The pH values in the working solutions were set in the range $8.5 \leq pH_m \leq 12$ (with $pH_m = -\log m_H$+). A last set of experiments was performed in 0.1 M Na_2CO_3 solutions as a function of [NaOH] = 0.01–0.6 M. Strongly reducing conditions ($pH_m + pe \leq 2$) were fixed for each independent solubility sample with $Na_2S_2O_4$, $SnCl_2$ or Fe powder. Uranium concentration, pH_m and E_h values were monitored at regular time intervals. Thermodynamic equilibrium was assumed after repeated measurements with constant [U] and pH_m. After attaining equilibrium conditions, selected uranium solid phases were characterized by XRD, SEM–EDS and XPS. These results are the basis for the development of new chemical, thermodynamic and activity models (SIT) for the system U(IV)–H^+–Na^+–CO_3^{2+}–HCO_3^-–OH^-–Cl^-–H_2O(l), which will be compared in this contribution to the available models for Th(IV) [3].

References

[1] D. Rai, A.R. Felmy, N.J. Hess, D.A. Moore, M. Yui, *Radiochim. Acta* **82**, 17-25 (1998).
[2] D.L. Clark, D.E. Hobart, M.P. Neu, *Chem. Rev.* **95**, 25-48 (1995).
[3] M. Altmaier, V. Neck, R. Müller, T. Fanghänel, *Radiochim Acta* **93**, 83-92 (2005).

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Study of zirconium dioxide dissolution and its surface reactivity in aqueous solution

Wiem Zouari, Tomo Suzuki-Muresan, Abdessalam Abdelouas, Bernd Grambow

SUBATECH, UMR 6457, Ecole des Mines de Nantes, 4 rue Alfred Kastler La Chantrerie, BP 20722, 44307 Nantes cedex 3
France

e-mail: wiem.zouari@subatech.in2p3.fr

Zirconium dioxide is an important material to be considered in the domain of nuclear waste management. It is for example considered as a potential candidate for host matrix for the disposal of actinides in a geological disposal vault, for the ‘burning of actinides’ in nuclear reactors and for the use of lanthanides as burnable-neutron absorbers to control the neutron flux in reactors. In case of direct disposal of spent nuclear fuel, ZrO_2 surface of the nuclear fuel cladding may come in contact with ground water. The solubility of zirconium oxide is very low ($<10^{-8}$M) [1-5] at pH>3, but uncertainties are high and the actual solubility value may differ by more than 6 orders of magnitude.

In this context, the objective of this work is to understand processes governing the equilibrium zirconium oxide/water and to study the surface reactivity of the material in contact with aqueous solutions.

To this purpose, the first step was to measure the solubility of well characterized ZrO_2 phases in order to understand parameters which control the solubility equilibrium. The solids characterizations have been done by XRD, BET, TEM and SEM. Dissolution of these solids was studied by approaching solubility from under-saturated to over-saturated conditions. To increase the solubility, acidic media was used (pH between 0 and 3). Concentrations of zirconium were determined by ICP-MS and HR-ICP-MS ([Zr] $\sim10^{-10} - 10^{-9}$ mol/L). Preliminary experimental results of equilibrium experiments and solids characterization will be presented.

Further experiments will be carried out to study the reactivity of different crystallographic faces of ZrO_2 put in contact with aqueous solutions. The challenge is to determine the highest reactive facets and to quantify the reactive sites on the solid surface. Furthermore, the dissolution kinetics depends on the energy of reactive sites. So, the final aim of the work is to model the solid/solution system to understand kinetics, mechanisms and reactive surface density involved in the dissolution processes.

References

[1] E. Curti, C. Degueldre, Solubility and hydrolysis of Zr oxides: a review and supplemental data. *Radiochimica Acta* **90**, 801-804 (2002).
[2] C. Ekberg, G. Kallvenius, Y. Albisson, P.L. Brown, Studies on the hydrolytic behaviour of zirconium (IV). *Journal of Solution Chemistry* **33**, 47-79 (2004).
[3] T. Kobayashi, T. Sasaki, I. Takagi, H. Moriyama, Solubility of zirconium (IV) hydrous oxides. *Journal of Nuclear Science and technology* **44**, 90-94 (2007).
[4] P.N. Kovalenko, K.N. Bagdasarov, Determination of zirconium hydroxide dissolution rate. *Zhur Nerorg. Khim.* **6**, 534-538 (1961).
[5] M.A. Pouchon, E. Curti, C. Degueldre, L. Tobler, The influence of carbonate complexes on the solubility of zirconia: new experimental data. *Progress in Nuclear Energy* **38**, 443-446 (2001).

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09:00	9:00 Opening 9:30 McKenzie	9:15 Marcus 9:35 Makino 9:55 Huang	9:15 González-Siso 9:35 Hefter 9:55 Pestova	9:15 Eckert 9:35 Leal	9:10 Lodge 9:30 Taki 9:50 Wang	09:00
10:00	10:15 Coffee break 10:45 Miron	10:15 Coffee break 10:45 Bendová	10:15 Coffee break 10:45 Matyskin	10:20 Coffee break 10:45 Pajarre	10:10 Coffee break 10:40 Poster winner/s	10:00
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