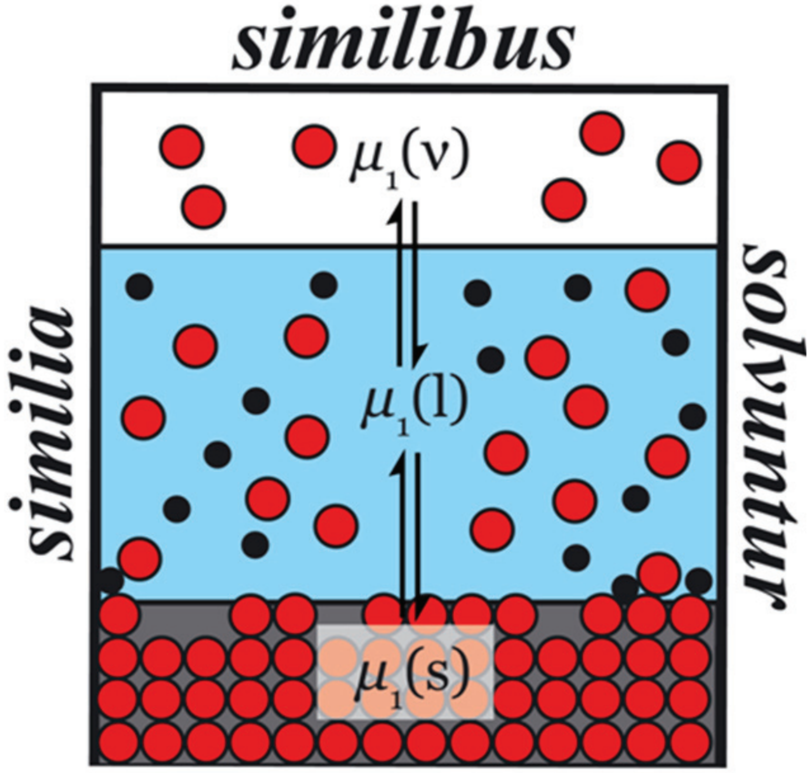
16th International Symposium on Solubility Phenomena and Related Equilibrium Processes

Karlsruher Institut für Technologie

ISSP 16



Karlsruhe Institute of Technology, Germany

July 21 - 25 2014

Abstract Volume

Preface

The International Symposium on Solubility Phenomena and Related Equilibrium Processes (ISSP) is an established bi-annual conference series organized by the IUPAC Subcommittee on Solubility and Equilibrium Data (SSED).

The Institute for Nuclear Waste Disposal (INE) of the Karlsruhe Institute of Technology (KIT) is honored to organize the 16th ISSP conference from July 21-25, 2014, in Karlsruhe, Germany. ISSP-16 is proud to follow a strong tradition of previous meetings held in different locations around the world:

1984	**1st**	**ISSP**	**London, ON Canada**
1986	**2nd**	**ISSP**	**Newark, NJ, New Jersey, USA**
1988	**3rd**	**ISSP**	**Guildford, Surrey, UK**
1990	**4th**	**ISSP**	**Troy, NY, USA**
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1994	**6th**	**ISSP**	**Buenos Aires, Argentina**
1996	**7th**	**ISSP**	**Leoben, Austria**
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2002	**10th**	**ISSP**	**Varna, Bulgaria**
2004	**11th**	**ISSP**	**Aveiro, Portugal**
2006	**12th**	**ISSP**	**Freiberg, Germany**
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2010	**14th**	**ISSP**	**Leoben, Austria**
2012	**15th**	**ISSP**	**Xining, China**
2014	**16th**	**ISSP**	**Karlsruhe, Germany**

ISSP conferences are gathering international experts on solubility studies to exchange new research and concepts. ISSP is addressing the general importance of solubility phenomena in a variety of settings ranging from green chemistry to nuclear waste disposal and many other modern technical applications. Specifically highlighting the importance of chemical thermodynamics and solubility studies both in fundamental and applied science, the conferences are featuring a wide agenda of topics. Accordingly, ISSP-16 includes invited and contributed oral and poster presentations ranging from basic equilibrium measurements to advanced theoretical predictions. ISSP-16 is offering a dedicated scientific platform for presenting, discussing and promoting the study of solubility phenomena and related equilibrium processes. Integrated into the ISSP-16 conference, a workshop on "Solubility and Speciation in Nuclear Waste Disposal" is held in order to highlight the key significance of solubility phenomena, aquatic chemistry and solution thermodynamics in this particular research field and application.

The organizers wish all participants a pleasant stay in Karlsruhe and fruitful exchange of scientific ideas and experience.

Organizing Committee
Karlsruhe, July 2014

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Karlsruhe Institute of Technology (KIT)
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Hermann-von-Helmholtz-Platz 1
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Content

Oral Presentations:

Poster

Oral contributions

Thermodynamic Properties of Molybdate Ion: Reaction Cycles and Experiments

Heinz Gamsjäger,[1] Masao Morishita[2]

[1]*Montanuniversität, Lehrstuhl für Physikalische Chemie, 8700 Leoben, Austria*
[2]*University of Hyogo, Department of Materials Science and Chemistry, Hyogo 671-2280, Japan*

Abstract

1. Standard Gibbs energy of molybdate ion

O'Hare et al. [1] derived $\Delta_f G^{\ominus}(\mathrm{MoO_4}^{2-}, 298.15\ \mathrm{K})$ using eq. (1):

$$\Delta_f G^{\ominus}(\mathrm{MoO_4}^{2-}) = -RT_{\mathrm{ref}} \ln K^{\ominus}_{s0} - n\Delta_f G^{\ominus}(\mathrm{M}^{2+/n}) + \Delta_f G^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) \qquad (1)$$

The most reliable values of $K^{\ominus}_{s0}$ have been determined for $\mathrm{Ag_2MoO_4}$(cr) and $\mathrm{BaMoO_4}$(cr). CODATA key values [2] are available for $\Delta_f G^{\ominus}(\mathrm{Ag}^+)$ and $\Delta_f G^{\ominus}(\mathrm{Ba}^{2+})$. One way to obtain standard Gibbs energies of formation for $\mathrm{Ag_2MoO_4}$(cr) and $\mathrm{BaMoO_4}$(cr) is by eqs. (2) and (3).

$$\Delta_f S^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) = S^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) - nS^{\ominus}(\mathrm{M, cr}) - 2S^{\ominus}(\mathrm{O_2, g}) - S^{\ominus}(\mathrm{Mo, cr}) \qquad (2)$$

$$\Delta_f G^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) = \Delta_f H^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) - T_{\mathrm{ref}}\Delta_f S^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) \qquad (3)$$

CODATA key values are available for $S^{\ominus}(\mathrm{Ag, cr})$, $S^{\ominus}(\mathrm{Ba, cr})$ and $S^{\ominus}(\mathrm{O_2, g})$, whereas values of $S^{\ominus}(\mathrm{Mo, cr})$ have been compiled and evaluated recently. Low-temperature heat capacity measurements of Morishita et al. [3] led to standard entropies of $\mathrm{Ag_2MoO_4}$(cr), $\mathrm{BaMoO_4}$(cr) and $\mathrm{SrMoO_4}$(cr). Standard enthalpies of formation for $\mathrm{Ag_2MoO_4}$(cr) and $\mathrm{BaMoO_4}$(cr) have been determined by solution calorimetry. $\Delta_f H^{\ominus}$ of alkaline earth molybdates has also been obtained by 3rd law analysis of high temperature equilibrium studies, but solution calorimetry values are preferable. Thus information is complete to apply eq. (1) for the analysis of silver and barium as well as strontium and calcium molybdates which finally results in a weighted mean value of $\Delta_f G^{\ominus}(\mathrm{MoO_4}^{2-}, 298.15\ \mathrm{K})$.

2. Standard enthalpy of molybdate ion

In principle $\Delta_f H^{\ominus}(\mathrm{MoO_4}^{2-}, 298.15\ \mathrm{K})$ can be obtained from eq. (4) analogous to eq. (1):

$$\Delta_f H^{\ominus}(\mathrm{MoO_4}^{2-}) = -R(\partial \ln K^{\ominus}_{s0} / \partial T^{-1})_p - n\Delta_f H^{\ominus}(\mathrm{M}^{2+/n}) + \Delta_f H^{\ominus}(\mathrm{M}_n\mathrm{MoO_4},\ \mathrm{cr}) \qquad (4)$$

Only $K^{\ominus}_{s0}$ of $\mathrm{Ag_2MoO_4}$(cr) has been measured in a temperature range which allows to calculate $(\partial \ln K^{\ominus}_{s0} / \partial T^{-1})_p$ reliably. The uncertainty of the values derived using eq. (4) is approximately ±4 $\mathrm{kJ \cdot mol^{-1}}$, thus $\Delta_f H^{\ominus}(\mathrm{MoO_4}^{2-}, 298.15\ \mathrm{K})$ determined by solution calorimetry of NaOH, $\mathrm{MoO_3}$(s) and $\mathrm{Na_2MoO_4}$(s) has been preferred.

3. Standard entropy of molybdate ion

Once standard Gibbs energy and standard enthalpy of $\mathrm{MoO_4}^{2-}$ is known the standard entropy is given by eqs. (5) and (6):

$$\Delta_f S^{\ominus}(\mathrm{MoO_4}^{2-}) = \left[\Delta_f H^{\ominus}(\mathrm{MoO_4}^{2-}) - \Delta_f G^{\ominus}(\mathrm{MoO_4}^{2-})\right] / T_{\mathrm{ref}} \qquad (5)$$

$$S^{\ominus}(\mathrm{MoO_4}^{2-}) = \Delta_f S^{\ominus}(\mathrm{MoO_4}^{2-}) + S^{\ominus}(\mathrm{H_2, g}) + 2S^{\ominus}(\mathrm{O_2, g}) + S^{\ominus}(\mathrm{Mo, cr}) \qquad (6)$$

This approach yields the most reliable value of $S^{\ominus}(\mathrm{MoO_4}^{2-}, 298.15\ \mathrm{K})$.

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E-mail address: gamsjaeg@unileoben.ac.at

Solubility and thermodynamic data for metal arsenates

Erich Königsberger,[1] Majzlan, Juraj[2], Nordstrom, D. Kirk[3]

[1] *Chemical and Metallurgical Engineering and Chemistry, Murdoch University, Murdoch, WA 6150, Australia*
[2] *Friedrich-Schiller-Universität Jena, Chemisch-Geowissenschaftliche Fakultät, Institut für Geowissenschaften, Carl-Zeiss-Promenade 10, 07745 Jena, Germany*
[3] *U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303, USA*

Abstract

Reliable and consistent thermodynamic data for arsenic minerals and aqueous species are required given the worldwide recognition of As poisoning in more than 70 countries [1] and the need to model As mobility more quantitatively in groundwater systems. Arsenic contamination can also constitute a serious problem in hydrometallurgical processing [2]. Unfortunately, few useful thermodynamic measurements have been made on reactions involving As minerals because of experimental difficulties, including long equilibration times with aqueous solutions, formation of metastable phases, and effects of crystallinity and particle-size on solubilities [3].

Solutions to these impediments are discussed in this review of solubility and thermodynamic data for Fe(III) [4] and Ca arsenates, and for solid solutions of arsenates with phosphates and vanadates [5]. We will present models for solubility calculations that utilize the most recent critical evaluation of the thermodynamic properties of arsenic species [6]. We will also make recommendations for the resolution of some discrepancies and suggest directions for further investigations.

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E-mail address: E.Koenigsberger@murdoch.edu.au

Multinuclear complex formation between Ca(II) and polyhydroxy carboxylates in hyperalkaline solutions relevant to radioactive waste disposal

Attila Pallagi,[1,2] Éva G. Bajnóczi,[1,2] Sophie E. Canton,[3] Trudy Bolin,[4]
Gábor Peintler,[2,5] Bence Kutus,[1,2] Zoltán Kele,[6] István Pálinkó,[2,7] Pál Sipos[1,2]

[1] *Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, H−6720 Dóm tér 7 (Hungary)*
[2] *Materials and Solution Structure Research Group, University of Szeged (Hungary)*
[3] *Department of Synchrotron Radiation Instrumentation, Lund University, PO Box 124, Lund, SE−221 00 (Sweden)*
[4] *Advanced Photon Source, Argonne National Laboratory, 9700 S Cass Ave, Lemont, IL 60439 (United States of America)*
[5] *Department of Physical Chemistry and Material Science, University of Szeged, Aradi Vértanúk tere 1, Szeged, H−6720 (Hungary)*
[6] *Department of Medical Chemistry, University of Szeged, Dóm tér 8, Szeged, H−6720 (Hungary)*
[7] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H−6720 (Hungary)*

Abstract

Alkaline solutions (pH > 13) containing polyhydroxy carboxylates and Ca(II) as the main metal ion component, are typical in cementitious radioactive waste repositories. Gluconate (Gluc$^-$) is a structural and functional representative of these sugar carboxylates. In this contribution, the structure and equlibria of complexes forming in such strongly alkaline solutions containing Ca^{2+} and gluconate will be presented, and the properties of these complexes will be compared with those formed between Ca(II) and organic ligands structurally related to Gluc$^-$, such as heptagluconate (Hglu$^-$) and gulonate (Gul$^-$).

The primary observation is, that Gluc$^-$ as well as Hglu$^-$ and Gul$^-$ significantly increases the solubility of portlandite ($Ca(OH)_2(s)$) under these conditions and Ca^{2+}-complexes of unexpectedly high stability are formed in a process involving the metal binding to deprotonated alcoholic OH group(s). For Gluc$^-$, the mononuclear (CaGluc$^+$ and [CaGlucOH]^0) complexes were found to be minor species in the pH- and concentration range employed for these studies, and predominant multinuclear complexes were identified. The formation of the neutral $[Ca_2Gluc(OH)_3]^0$ ($\log \beta_{213} = 8.03$) and $[Ca_3Gluc_2(OH)_4]^0$ ($\log \beta_{324} = 12.39$) has been proven via H_2/Pt-electrode potentiometric measurements and was confirmed *via* XAS, multinuclear NMR, ESI-MS, conductometry and freezing-point depression experiments. The binding sites of Gluc$^-$ were identified from multinuclear NMR measurements. Beside the carboxylate group, the O atoms on the second and third carbon atoms were proved to be the most probable sites for Ca^{2+} binding.

Polynuclear Ca^{2+} complexes are present in hyperalkaline solutions of Hglu$^-$ and Gul$^-$ too, thus the phenomenon of polynuclear complex formation with Ca^{2+} at high pH seems to be a common feature of polyhydroxy carboxylates. The ligands shown here and isosaccharinate (ISA$^-$). Therefore, these observations are of relevance in the thermodynamic modeling of radioactive waste repositories, where the predominance of the binuclear Ca^{2+}-complex which is a precursor of various high stability ternary complexes is also demonstrated.

Acknowledgements

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E-mail address: sipos@chem.u-szeged.hu

Complexation of An(III) and An(IV) with gluconate under hyperalkaline pH conditions: solubility and TRLFS studies

X. Gaona,[1] H. Rojo,[1,2] T. Rabung,[1] M. García-Gutiérrez,[3] T. Missana,[3] M. Altmaier[1]

[1]*Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe (Germany)*
[2]*Laboratory for Waste Management, Paul Scherrer Institut, Villigen PSI, Switzerland*
[3]*CIEMAT, Research Centre for Energy, Environment and Technology, Madrid, Spain*

Abstract

Radionuclide solubility and sorption in cementitious and saline systems can be affected by the presence of organic ligands. Gluconic acid ($C_6H_{12}O_7$, HGH_5) is a poly–hydroxocarboxylic acid expected in repositories for low and intermediate–level radioactive waste (LILW) as component of cementitious materials. The formation of very stable An(III/IV)–gluconate complexes has been reported in the literature. In the case of An(IV), the stability of these complexes can be further increased in the presence of Ca^{2+} due to the formation of ternary Ca–An(IV)–gluconate complexes. On the contrary, no such ternary species have been described so far for An(III). The development of complete and correct chemical, thermodynamic and activity models for the ternary systems Ca–An(III/IV)–gluconate for dilute to concentrated $CaCl_2$ solutions is thus required to properly assess the impact of this ligand on the mobilization of An(III) and An(IV) under repository-relevant conditions.

Undersaturation solubility studies with $Nd(OH)_3(am)$ were conducted in dilute NaCl (0.1 M) and $CaCl_2$ (0.1 and 0.25 M) solutions. Parallel experimental series were prepared at pH_c ~12 with $10^{-6} \le [GH_5^-] \le 10^{-2}$ M, and $[GH_5^-] = 10^{-3}$ M with $9 \le pH_c \le 13$. $[Nd]_{aq}$ was quantified by ICP–MS after 10 kD ultrafiltration, whereas $[GH_5^-]_{tot}$ in solution was measured as total organic carbon. Solid phases were characterized by XRD. TRLFS measurements were performed with 10^{-7} M Cm(III) per sample in the same matrix solutions. The initial concentration of gluconate in all samples (10^{-6} M) was increased to 3×10^{-3} M by step–wise additions of $NaGH_5$–NaCl or $Ca(GH_5)_2$–$CaCl_2$ solutions. Np(IV) was obtained by chemical reduction of a Np(V) stock solution with $Na_2S_2O_4$ at pH = 8, and quantitatively precipitated at $pH_m = 12$ as $NpO_2(am,hyd)$. The resulting solid phase was divided in different samples (~2 mg ^{237}Np per batch experiment) with 0.1–3.5 M $CaCl_2$ as background electrolyte, with $10^{-6} \le [GH_5^-]_{tot} \le 10^{-2}$ M and $9 \le pH_m \le 12$. All samples were prepared and stored in Ar gloveboxes under exclusion of O_2 and CO_2.

The solubility of $Nd(OH)_3(am)$ remains unaffected by gluconate in 0.1 M NaCl solutions. XRD and TOC analyses confirm that no secondary (crystalline) solid phases are forming and that all gluconate remains in solution under these conditions. On the other hand, the solubility of $Nd(OH)_3(am)$ in 0.1 and 0.25 M $CaCl_2$ solutions is clearly increased by gluconate under hyperalkaline conditions. The species forming are pH–dependent and in all cases involve the coordination of Ca^{2+}. Slope analysis of $Nd(OH)_3(am)$ solubility under increasing gluconate concentration (log [Nd] *vs.* log $[GH_5^-]_{tot}$) likely indicates the formation of a Nd–gluconate complex with stoichiometry 1:2. At $[GH_5^-]_{tot} \ge 10^{-3}$ M, no further increase of the Nd(III) concentration is observed, resulting in an upper solubility limit at [Nd] ~$10^{-6.5}$ M which could indicate the formation of a new Ca–Nd(III)–gluconate solubility limiting solid phase. TRLFS shows the formation of one main Cm(III)–gluconate species in NaCl systems at 10^{-3} M $\le [Ca]_{tot} \le 10^{-2}$ M. Consistent with Nd(III) solubility data, TRLFS confirms the key role of Ca^{2+} in the complexation process and likely formation of a ternary Ca–Cm(III)–gluconate complex with Ca:gluconate ratio 1:1. At least two further Ca–Cm(III)–gluconate species are identified in 0.1 M and 0.25 M $CaCl_2$ solutions by TRLFS, pointing to a very complex chemistry and speciation for this system. Weaker Cm(III)–gluconate complexes are also observed by TRLFS in the absence of Ca.

The presence of gluconate induces a significant increase on $NpO_2(am,hyd)$ solubility in $CaCl_2$ solutions. This increase is stronger at higher concentrations of Ca^{2+}, thus suggesting the formation of ternary complexes analogous to those described in the literature for Th(IV) ($CaAn^{IV}(OH)_4(GH_5)_2(aq)$). Independent of $[CaCl_2]$, the system reaches a saturation level at [Np] ~$10^{-5.5}$ M. As for Nd(III), this observation could be explained by the formation of a new Ca–Np(IV)–gluconate solid phase, although this hypothesis remains to be further confirmed by appropriate solid phase characterization (XRD, SEM–EDS) currently under way.

These results indicate that gluconate has a clear but limited impact on the solubility of An(III) and An(IV) under repository-relevant conditions. In both cases, the possible formation of a ternary Ca–An–gluconate solid phase could be considered as a potential mechanism for the retention of actinides at elevated gluconate concentrations.

E-mail address: xavier.gaona@kit.edu

Modeling Speciation and Solubility in Systems Containing Actinides

Peiming Wang, Andrzej Anderko

OLI Systems, Inc., 240 Cedar Knolls Road Suite 301, Cedar Knolls, NJ 07927, U.S.A.

Abstract

Aqueous speciation and solubility of actinides are of particular interest in nuclear fuel recycling processes. They are also among the most fundamental issues for geochemical modeling with regard to the safety of nuclear waste disposal. The chemical behavior of the radionuclides in these processes strongly depends on the conditions under which their chemical forms may change due to hydrolysis, complexation, and formation of solid phases. Detailed knowledge and reliable information on the chemical speciation of actinides in solution and their solubility equilibria are indispensable for developing efficient technologies in nuclear fuel processing and for predicting the fate of radioactive components for the safety assessment of nuclear waste management.

In the present work, we apply a previously developed thermodynamic model, referred to as the Mixed-Solvent Electrolyte (MSE) model[1] to calculate the solubility and speciation in selected actinide systems. Specifically, solubilities and chemical speciation of uranium and plutonium systems containing nitric acid up to high concentrations are analyzed as they represent systems for nuclear fuel processing applications. In addition, chemistry of americium is investigated as an application example for elucidating how the radionuclides in a natural aquatic system or a nuclear waste depository can be stabilized by solid-liquid equilibria and by changing conditions such as partial pressure of CO_2, pH, and concentrations of carbonate and chloride. Selected results are shown in Figs 1 and 2. Additional results will be demonstrated and discussed.

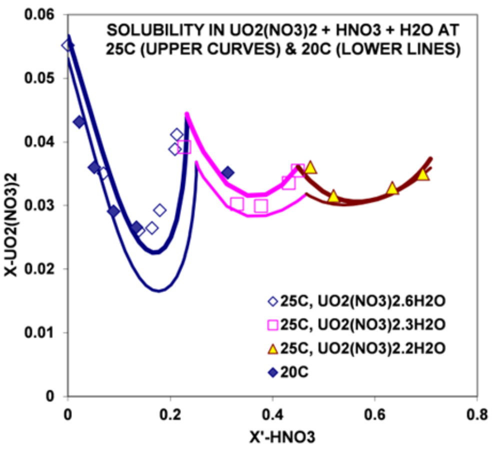

Fig. 1. Solubility in U(VI)+HNO_3+H_2O system[2]

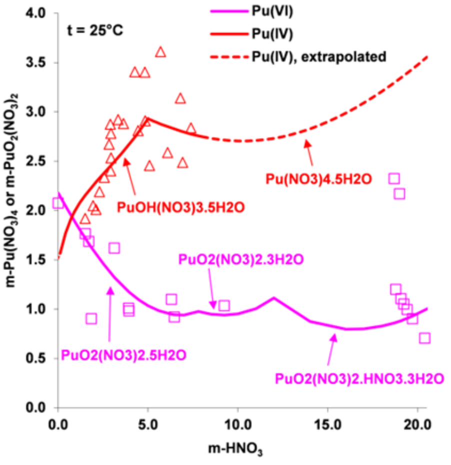

Fig. 2. Solubility of Pu(VI) and Pu(IV) in HNO_3+H_2O solutions[3]

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E-mail address: pwang@olisystems.com

Radium solubility in the presence of barite: a combined experimental and atomistic modelling approach

Felix Brandt,[1] Martina Klinkenberg,[1] Victor Vinograd,[2] Konstantin Rozov,[1]
Uwe Breuer,[3] Dirk Bosbach[1]

[1]*Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research –*
Nuclear Waste Management and Reactor Safety (IEK-6), 52425 Juelich, Germany
[2]*Institute of Geosciences, Goethe University, Altenhöferallee 1, 60438 Frankfurt, Germany*
[3]*Forschungszentrum Jülich GmbH, Central Institute for Engineering,*
Electronics and Analytics (ZEA-3), 52425 Juelich, Germany

Abstract

^{226}Ra is an important source of technically enhanced naturally occurring radioactive materials (TENORM). Furthermore, in some scenarios for the safe disposal of spent nuclear fuel, ^{226}Ra has been identified as a relevant contributor to the long-term radiotoxicity. Thermodynamic calculations indicate that the formation of solid solutions can reduce the Ra solubility by several orders of magnitude compared to the solubility of pure $RaSO_4$ [1, 2]. However, due to a lack of reliable thermodynamic and experimental data for the expected scenario at close-to equilibrium conditions, the solid solution system $RaSO_4$-$BaSO_4$-H_2O has so far not been considered in long term safety assessments for nuclear waste repositories.

Here we have combined a macroscopic experimental approach with atomistic calculations and thermodynamic modeling to study in detail how a Ra containing solution will equilibrate with solid $BaSO_4$ at room temperature. Batch recrystallization experiments were carried out with two types of barite at an initial Ra/Ba ratio of 0.3 (5×10^{-6} mol/L Ra) at near neutral pH-conditions and with two different solid/liquid ratios (0.5 and 5 g/L). Depending on the solid/liquid ratio, a significant decrease of the Ra concentration by more than 99 % occurred within the first 70 days of the experiment. A final steady state was reached after more than 800 days for all experiments.

The thermodynamic mixing parameters for the solid solution have been derived from the change in the total energy of a $2 \times 2 \times 2$ supercell of barite due to the insertion of a single substitutional defect of radium into the barite structure. The computed value of $W_{BaRa} = 2.50 \pm 1.00$ kJ/mol implies a non-ideal solid solution.

The results of thermodynamic modeling indicate a good agreement of the observed experimental Ra solubility in contact with a $(Ra,Ba)SO_4$ solid solution after more than 800 days with the computed W_{BaRa} and a theoretical solubility of the $RaSO_4$ endmember of $\log K_{SP}(RaSO4) = -10.41$. These thermodynamic parameters for the solid solution can now be applied in the safety assessment of the direct disposal of spent fuel elements.

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E-mail address: f.brandt@fz-juelich.de

Solubility seen from an environmental chemist point of view: caveats and needs

Montserrat Filella

Institute F.-A. Forel, University of Geneva, Route de Suisse 10, Ch-1290 Versoix, Switzerland

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Abstract

Solubility-based considerations are often absent or not correctly-applied in environmental chemistry and ecotoxicology. The subject of the solubility of ionic compounds in waters is discussed in general chemistry textbooks, typically within the first several chapters. The subject is also presented in any Environmental Chemistry book. Unfortunately, the treatment used is often too simplistic, when not openly misleading. In the case of general textbooks the problem has often been discussed in the Journal of Chemical Education; in the environmental field is not so largely acknowledged. In practice, the gap between needs and tools is big. Different practical cases that illustrate the relevance, but also the difficulty, of applying sound solubility principles to environmental problems will be discussed:

1. The common obliviousness of solubility considerations in ecotoxicological experiments; the case of Sb biomethylation experiments (Filella and Williams, 2010).
2. The blind use of ready-made calculation methods; the case of the estimation of CO_2 fluxes in freshwaters in climate-change related studies.
3. The role of biota; the case of the recently detected Ba- and Sr-rich spherules in freshwaters (Lake Geneva) in conditions of undersaturation (Jaquet et al., 2013).
4. Solubility versus sorption; the case of antimony-iron oxide interactions.

'Real' physico-chemists might look at the problems discussed here as being exclusively derived from insufficient training and be tempted to qualify current practice as 'bad science' (which indeed might be in some cases the case). However, this attitude, anchored on a personal scientific practice centred on rigorous lab experiments and calculations, would ignore their responsibility in ensuring a better transmission of knowledge across disciplines as well as the complexity of environmental systems. Mineralogists and some geochemists will probably feel closer to environmental caveats but might miss the weight of kinetics (i.e., relatively short time processes) and biota in environmental processes. Discussions on these issues will be encouraged and welcome.

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Acknowledgements

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E-mail address: montserrat.filella@unige.ch

Chloride versus sulphur control on palladium transport by hydrothermal fluids

Elena F. Bazarkina,[1,2] Gleb S. Pokrovski,[3] Jean-Louis Hazemann[4]

[1]Institute of Geology of Ore Deposits, Mineralogy, Petrography and Geochemistry,
Russian Academy of Sciences, Staromonetny per. 35, 119017 Moscow, Russia
[2]GeoRessources, Université de Lorraine, CNRS, BP 70239, F-54506 Vandoeuvre-lès-Nancy, France
[3]Expérimental Geochemistry of Ore Deposits, Géosciences Environnement Toulouse,
GET - University of Toulouse - CNRS - IRD - OMP, 14, avenue E. Belin, F-31400 Toulouse, France
[4]Institut Néel, CNRS, 25, avenue des Martyrs, F-38042 Grenoble Cedex 9, France

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Abstract

Although palladium (Pd) has a very low average abundance in the crust (~1 ppb), it may be concentrated to economic levels (~ppm) in some hydrothermal processes [e.g., 1]. The present study is aimed at better understanding the causes of this enrichment and, in particular, at quantifying Pd speciation in Cl-bearing hydrothermal fluids. In situ X-ray absorption spectroscopy was used to reveal the identity, structure and stability of Pd aqueous species in model (Na,Li)Cl-HCl-HNO_3-$HClO_4$-H_2O solutions and to measure the solubility of PdO(s) and PdS(s) at temperatures (T) up to 450°C and pressures (P) of 600 bar.

In Cl-free HNO_3/$HClO_4$ solutions, the square planar $Pd(H_2O)_4^{2+}$ cation with an average Pd-O distance of 2.00±0.01 Å is the dominant Pd form at 30-100°C. At T > 100°C, this cation undergoes hydrolysis resulting in Pd precipitation. In Cl-bearing solutions Pd forms square planar $PdCl_n(H_2O)_{4-n}^{2-n}$ complexes (where $1 < n < 4$) with Pd-O and Pd-Cl distances of 2.00-2.10 and 2.26-2.31 Å, respectively. At 30-250°C our data are consistent with a mixture of four complexes, $PdCl(H_2O)_3^+$, $PdCl_2(H_2O)_2^0{}_{(aq)}$, $PdCl_3(H_2O)^-$, and $PdCl_4^{2-}$, but above 250°C $PdCl_3(H_2O)^-$ and $PdCl_4^{2-}$ are largely dominant over a wide range of Cl concentrations, from 0.03 to at least 9 mol/kg H_2O. Spectroscopic analyses of the species distribution allowed derivation of the stability constant of the reaction $PdCl_3^- + Cl^- = PdCl_4^{2-}$ from 300 to 450°C and 600 bar. The chloride speciation of Pd is very similar to that of base and associated metals [2; references therein].

Combination of these data with in-situ measured solubility of PdO(s) and PdS(s) in the same fluids allowed generation of a self-consistent thermodynamic data set in the system PdS(s)-PdO(s)-$PdCl_3^-$-$PdCl_4^{2-}$. Thermodynamic modeling using these new data indicates that Pd can be significantly mobilized as chloride complexes only in sulfide-free oxidizing geological settings in which PdO(s) or Pd(s) are solubility-controlling phases. By contrast, at typical pH (4-8), chlorinity (<10-15 wt% NaCl) and H_2S contents (0.001-1 wt%) of most hydrothermal fluids, the absolute concentration of Pd-Cl complexes is too low to explain Pd enrichment in volcanogenic massive sulfide, modern seafloor sulfide, and porphyry Cu-Au-Mo deposits. The very low PdS(s) solubility is the major factor limiting Pd mobility in these systems. As a result, other, probably S-bearing, complexes are likely to control Pd transport in such settings. The identity and stability of such species await further studies.

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E-mail address: elenabaz@igem.ru

Rare earth metals leaching and recovery from igneous sources

Justin Salminen, Lea Räsänen, Jarno Mäkinen, Juha Kaunisto, Pertti Koukkari

VTT Technical Research Centre of Finland, Biologinkuja 7, 02044, Espoo, Finland

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Abstract

Rare Earth metals containing material from igneous rock sources were studied in this work.

Leaching and recovery from leachate are discussed and different REE recovery extraction processes are summarized.

Apatites, which are the main source of phosphoric acid and phosphate fertilizers, are occasionally found to contain significant amounts of rare earth elements and can be used as sources for rare earth elements. Leaching of rare earth elements from apatite was carried out in a standard reactor consisting with aeration, redox measurement, and a pH titration unit. Leaching rates were defined for dissolved species. Results show high yields for most of the REE elements found in the starting material.

Laboratory scale liquid-liquid extraction tests were carried out for REE elements recovery from the leachate and from synthetic solution. Different extraction agents were used including generic hydrophobic ionic liquids, bis(2-ethylhexyl)phosphoric acid (DEHPA), and kerosene. Distribution coefficients were defined for REE elements and impurities. Process assessment and technology development are discussed.

E-mail address: justin.salminen@vtt.fi

Solubility of strontium arsenates

M. Clara Magalhães,[1] Catarina Martins,[2] Catarina Barbosa[1]

[1]*Department of Chemistry and CICECO, University of Aveiro, P-3810-193 Aveiro, Portugal*
[2]*Institut für Materialchemie, Technische Universität Wien, Karlsplatz 13, 1040 Wien, Austria*

Abstract

Arsenic is becoming a world environmental problem. Crystallization of arsenic containing solid phases can be a process to ensure arsenic geological long-term immobilization in the environment. It is known that solid phases containing lead and arsenate ions belonging to the *apatite*-group are among the less soluble known species [1]. In order to find other stable solid phases containing arsenates, with low solubility in aqueous solutions at the standard pressure, average environmental temperatures between 18 and 25 ºC, and pH between 6 and 8.5, studies where conducted with strontium arsenates. The choice was based on the fact that strontium(II) ions have ionic radius similar to lead(II) ions [2], and assuming that the relation between the anionic and cationic radii is an important parameter in the formation and stability of solid phases. Solid strontium arsenates where synthezised and their stability in aqueous solutions was studied.

In order to find the most stable strontium arsenate solid phases, under the environmental conditions of a temperate climate, the synthesized solids were left to equilibrate with the mother solutions, with ionic strengths between 0.1 and 0.4 mol/L, for periods ranging from three days to eight months, at 25 ºC, and sea level atmospheric pressure. By X-ray diffraction were identified solid phases with the following composition: $SrHAsO_4$, $SrHAsO_4 \cdot H_2O$, $Sr_5(AsO_4)_3OH$, $Sr_5(AsO_4)_3Cl$, and two new solid phases still under identification. Solubility data of the above mentioned solid phases will be presented and data will be analyzed together with the data already existing for calcium and lead arsenates with similar compositions.

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E-mail address: mclara@ua.pt

CO_2 capture systems with liquid-liquid phase split in addition to VLE and SLE

Kaj Thomsen, Muhammad Waseem Arshad

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

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Abstract

A comprehensive database consisting of 1500 experimental data points for freezing point depression, CO_2 solubility, vapor pressure, heat of absorption, and liquid-liquid equilibrium in the system DEEA-MAPA-CO_2-water was compiled by combining own measurements with data from literature.

DEEA is a tertiary amine (2-(diethylamino)ethanol). MAPA is 3-(methylamino)propylamine and has a primary and a secondary amine group. The possible formation of MAPA carbamate and di-carbamate gives rise to a fast reaction between DEEA-MAPA-CO_2-water solutions and gaseous CO_2.

Liquid-liquid phase splits are occurring in DEEA-MAPA-CO_2-water solutions with high CO_2 loadings. This liquid-liquid phase split can be an advantage for CO_2 capture processes. The loaded solutions split into two aqueous phases of which one is rich in MAPA and CO_2, while the other is rich in DEEA. Only the aqueous phase rich in MAPA and CO_2 needs to pass through the desorber for the release of CO_2. After the desorber, the aqueous DEEA phase and the aqueous MAPA phase are re-combined and re-used for absorption.

Due to the formation of protonated forms of DEEA and MAPA, di-protonated MAPA, carbamate and di-carbamate of MAPA, and protonated forms of MAPA carbamates, this system is quite complicated to model thermodynamically. The system was modeled using the Extended UNIQUAC model for electrolytes. 94 model parameters and six thermodynamic properties were determined in the modeling. The model was found to represent the experimental data with a very satisfactory accuracy with a single set of parameters for all types of data. A result for liquid-liquid equilibrium is shown in figure 1.

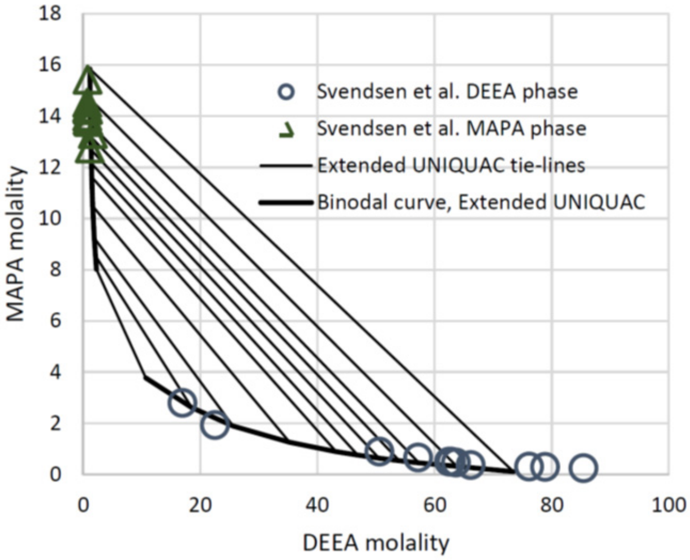

Figure 1: *LLE in CO_2-MAPA-DEEA-H_2O solutions at 80°C. Experimental data from Svendsen et al.[1]. Calculated values for solution with 7.5 molal MAPA solution with 0.45 mol CO_2/mol MAPA. Varying DEEA molality.*

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E-mail address: kth@kt.dtu.dk

Effect of the addition of $LiNO_3$, LiI and LiCl in the solubility of LiBr aqueous solutions for absorption refrigeration systems

Javier Mesones, Daniel Salavera, Alberto Coronas

Group of Applied Thermal Engineering – CREVER
Department of Mechanical Engineering. Universitat Rovira i Virgili, Avda Paisos Catalans 26, 43007 Tarragona, Spain

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Abstract

Some studies with new absorbents [1-4] have been carried out to improve the solubility of the conventional H_2O/LiBr mixture, used in absorption chillers for air-conditioning applications, in order to avoid crystallization in systems with air-cooled absorbers, which involves higher absorbent concentrations. Recently, some authors [5-10] have considered the lithium salts mixture proposed by Koo et al. [4] as a good alternative to improve the solubility and corrosiveness of the conventional mixture. Consequently, they studied its thermophysical properties and the heat/mass transfer performance in the absorber. However, this mixture should be discussed and reconsidered because some aspects, as the solubilty for more concentrated solutions than 62.5 % in salt mass fraction or the effect of the addition of LiCl to the solubility of the mixture, were not taken into account.

The aim of this work is to accomplish an extension of the solubility study of Koo et al. [5] analysing by visual-polythermal method how affects to the solubility of H_2O/LiBr the separate addition of lithium salts $LiNO_3$, LiI and LiCl at different mole salt ratios and salt mass fractions from 65 % to 69 %, in order to achieve an optimum salt ratio that obtains the minimum solubilility temperature of the mixture.

The addition of $LiNO_3$ obtained an optimum $LiNO_3$/LiBr mole ratio of 0.143. Fixed the optimum mole ratio $LiNO_3$/LiBr, the addition of LiI showed an optimum LiI/$LiNO_3$ ratio of 0.5. Finally, fixed the optimum ratios obtained previously, the addition of LiCl showed an optimum LiCl/LiI mole ratio of 0.25. Therefore, from the point of view of solubility, the optimum mole salt ratio of the mixture H_2O/LiBr+$LiNO_3$+LiI+LiCl proposed is 7:1:0.5:0.15.

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E-mail address: alberto.coronas@urv.cat

Solute-solvent interactions with COSMO-RS: Investigation of the solubility of a UV-Filter, avobenzone, in cosmetic oils

Adrien Benazzouz, Laurianne Moity, Valérie Molinier, Jean-Marie Aubry

Université Lille Nord de France, E 4478 Chimie Moléculaire et Formulation, Cité scientifique, Bâtiment C6, 59652 Villeneuve d'Ascq, France

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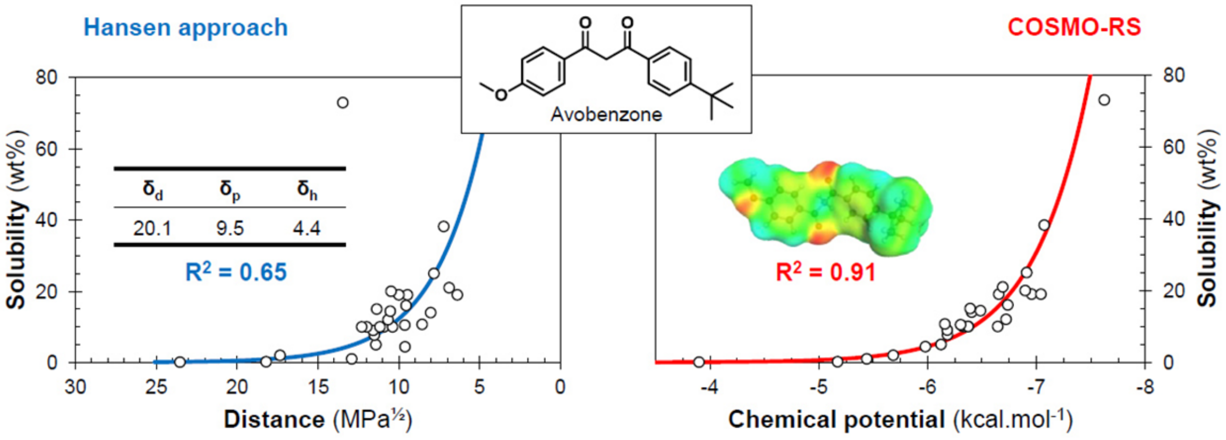
Abstract

To widen the range of applications of solvents and particularly emerging sustainable solvents, tools are needed for the fast assessment of their solubilizing properties. Hansen's approach is the most popular one wherein solvents are described by 3 parameters corresponding to dispersion, polar and hydrogen bonding interactions [1]. The main methods to predict the values of Hansen solubility parameters are based on group contributions and thus fail in the description of complex molecules. Alternatively, the COnductor-like Screening MOdel for Real Solvents (COSMO-RS) is a quantum chemical prediction model that considers molecules in their liquid states, allowing the estimation of a wide range of properties from the mere knowledge of the molecular structure [2], thus making *a priori* description of the solvent behavior [3].

The solubility of avobenzone – a key organic UV filter used in sunscreen formulations – in a series of solvents is investigated thanks to the Hansen's approach. The coordinates of the Hansen solubility sphere of avobenzone were experimentally determined, allowing the identification of its solvents and non-solvents in reasonable agreement with the solubility values, even if strong outliers were identified. COSMO-RS is then used to rationalize these results, providing reliable and more accurate solubility predictions *via* the calculation of the chemical potential. In particular, it offers a new light on solubility by going beyond the old alchemical maxim "*similia similibus solvuntur*" with the evidence of a different solubilizing behavior: "opposites attract" [4].



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E-mail address: adrienbenazzouz@aol.com

The OECD Nuclear Energy Agency Thermochemical Database Project

Maria-Eleni Ragoussi

Nuclear Energy Agency (NEA), Organisation for Economic Co-operation and Development (OECD)
12, boulevard des Îles, 92130 Issy-les-Moulineaux, France

Abstract

The OECD Nuclear Energy Agency (NEA) Thermochemical Database Project aims at producing a high quality chemical thermodynamic database of selected elements, important in radioactive waste management. The preparation of this database follows strict guidelines[1] to assure the consistency, reliability and CODATA-compatibility of the data provided, as well as to meet the specialized modeling requirements for safety assessments of radioactive waste disposal systems. This oral contribution will describe the bases, scientific principles and organization of the TDB project, together with its evolution from its inception in 1984 to the present organization as a semi-autonomous project under the aegis of the OECD NEA. The work carried out has resulted in the publication of eleven major *reviews* on the chemical thermodynamics of *inorganic* species and compounds of U, Np, Pu, Am, Tc, Ni, Se, Zr, Th, Sn and Fe, one 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.[2] Currently, three reviews are in development, namely Fe (2nd volume), Mo and the auxiliary data, in addition to two state-of-the-art reports on cements and high ionic strength systems respectively. Lastly, the 4th phase of the TDB project was completed in January 2014 and the 5th phase is in the process of entering into force.

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E-mail address: maria-eleni.ragoussi@oecd.org

Prediction of the solubility of organic solutes in aqueous electrolytes

Yizhak Marcus

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

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Abstract

The solubility of an organic solute (subscript $_{N}$) in water, s_{N0}, can be calculated by means of well known linear solvation energy relationships (LSER), such as those of Kamlet and Taft, Yalkowski et al, Abraham and Le, among others. Given the value of s_{N0}, what would be its solubility, s_N, in the presence of an electrolyte (subscript $_{E}$, or a mixture of electrolytes, such as sea water) at a concentration c_E?

This question can be answered [1] in terms of the Setchenow constant k_{NE}:

$$s_N = s_{N0} \cdot ln(10) \cdot exp(-k_{NE}c_E)$$

The Setchenow constant, in turn, can be predicted from two properties of the solute and two properties of the (ions of the) electrolyte. The resulting expression is:

$$k_{NEpred} = 0.10 - 10^{-4}(2.0 + 0.729V_x - 6.6\delta_H)\Sigma_I \nu_I \Delta V_I^{conv}$$

The solute properties are its McGowan volume V_x and its Hildebrand solubility parameter δ_H. The McGowan volume is:

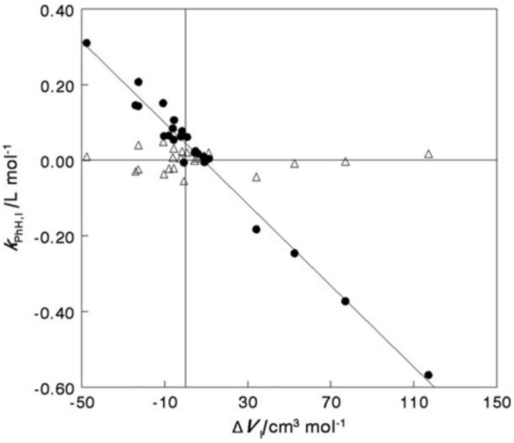
$$V_x = \Sigma n_{atom\text{-}j}V_{x\text{-}j} - 6.56n_{bonds}$$

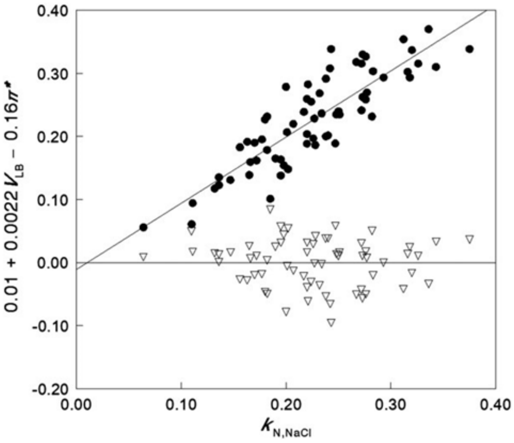
where n denotes the number of atoms of kind j, the volume of each being $V_{x\text{-}j}$, and the number of bonds between the atoms. The electrolyte properties are additive for the ions (subscript $_{I}$): $c_E = \Sigma \nu_I c_I$, with ν_I being the stoichiometric coefficients, and:

$$\Delta V_I^{conv} = V_I^{\infty\, conv} - V_{intr}$$

Here $V_I^{\infty\, conv}$ is the standard partial molar ionic volume on the convention that $V_I^{\infty}(H^+,aq) = 0$ and V_{intr} is the intrinsic ionic volume.

All the required properties are known for many solutes and ions, as are the experimental solubilities in the aqueous electrolyte solutions. The predicted solubilities agree with the experimental ones within the scatter of the latter (empty symbols are deviations).





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E-mail address: ymarcus@vms.huji.ac.il

Accounting for aqueous- solid solution interaction kinetics in computer-aided calculations of partial equilibria

Dmitrii A. Kulik, Bruno M.J. Thien, Enzo Curti

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

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Abstract

Experimental data indicate that the minor element partitioning during mineral precipitation or dissolution usually deviates from the complete aqueous- solid solution equilibrium. Such phenomena can be appropriately modeled by invoking the principle of *partial equilibrium*, which also allows changes in amount and composition of an *overgrowth* (solid solution) phase as function of time to be linked to the surface area or volume of a *substrate* phase (seed or adsorbent) forming a *layered composite*. The substrate can equilibrate with the aqueous solution or can be metastable when covered by the overgrowth. Kinetic rates are scaled to the outer surface area of the composite, which varies with time during the process.

Selected mineral-aqueous reaction kinetic laws plus the "unified uptake kinetics model" (UUKM) [1] describing trace element uptake by coprecipitation, have been implemented in the TKinMet C++ code library both for spatially separated or metastability-linked (layered) solid solution phases. TKinMet is an extension of GEMS3K and GEM-Selektor codes for chemical thermodynamic modelling [2]; it is designed similar to the TSolMod C++ code library for models of (non-ideal) mixing in phases-solutions [2] with the goal of keeping the GEM algorithm independent of physicochemical features of phases and their components.

The new implementation was tested on simple experimental systems, including the precipitation kinetics of portlandite and calcite, as well as the Sr and Cd uptake in calcite. Some chemically important effects were clearly demonstrated, e.g. the change of trace element partitioning upon variation of precipitation rates, temperature, and precipitation-induced depletion of the components from the aqueous phase in closed- and semi-open systems. The capability of modelling such effects overcomes strict limitations of previously published uptake kinetics models [3], which require constant aqueous solution composition and constant growth rate.

The TKinMet library makes the GEM software an efficient and versatile modelling tool of potentially wide applicability in aquatic chemistry, chemical engineering, and waste geochemistry. Future work will concentrate on studying back-coupling and time-stepping artefacts in kinetically driven simulations; further verification of TKinMet functionality for more complex systems and processes such as the recrystallization of sulphates with uptake of radionuclides; on surface precipitation of solid solutions on goethite or other environmentally relevant substrates; and on the impact of nucleation on trace element partitioning.

The research leading to these results has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Program FP7-Fission-2010 under grant agreement number 269688 (CP-SKIN).

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E-mail address: dmitrii.kulik@psi.ch

Designing a solubility database for reactive systems

Darren Rowland, Erich Königsberger, Peter May

[1]*Chemical and Metallurgical Engineering and Chemistry, Murdoch University, South St, Murdoch 6150, Australia*

Abstract

At the present state-of-the-art, the modelling of equilibria occurring in concentrated reactive electrolyte mixtures remains problematic: the theoretical deficiencies related to calculating the activity of species in multicomponent solutions seem unlikely to be overcome soon. However, thermodynamic data for reactive systems, e.g. solubility values, are widespread in the chemical literature and need to be better utilised.

A key challenge for storing this information is expressing the complete chemistry of a large number of potentially complicated solutions – such as phosphate and borate buffers – in a compact, and ultimately machine-processable, form. The approach taken to date (e.g. [1]) records only the analytical concentrations of well-defined components. We are seeking to build the data repository which will be required in future to parameterise theoretical solution chemistry frameworks estimated to involve at least five million experimental data values.

A major issue is that existing databases do not store information relating to the chemical behaviour of the solution components that is needed for processing experimental data. We find that defining all solution species and the set of allowed reactions is necessary and sufficient for describing the chemistry of the solution.

A database system implementing this design is in development building upon our existing chemical reaction [2] and physicochemical property [3] databases. Accordingly, the new database can store a vast range of properties including solubility, pH, density, mean activity coefficients and equilibrium constants. Methods to harmonise these data, which is a preliminary step prior to extracting reliable thermodynamic parameters for modelling, are described.

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E-mail address: d.rowland@murdoch.edu.au

GEMSFITS: A code package for input parameter optimization of chemical thermodynamic models

George D. Miron,[1] Dmitrii A. Kulik,[2] Svitlana V. Dmytrieva,[3] Thomas Wagner[4]

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

Abstract

The GEMSFITS code package is a tool for regressing internally consistent input parameters of chemical thermodynamic models against experimental data, and for performing various inverse-modeling tasks (e.g. geothermobarometry). This has many applications for more accurate and robust modeling of complex multicomponent-multiphase geochemical systems. The new code is more general and has a much broader scope than its earlier prototype[1] aimed at fitting interaction parameters of thermodynamic activity models only. The GEMSFITS codes include the `GEMS3K` chemical solver[2] – a Gibbs energy minimization kernel of GEM Software that includes the `TSolMod` library[3] of equations of state and activity models of solution phases (fluid mixtures, aqueous solutions, solid solutions etc.). For parameter fitting, GEMSFITS codes use a robust open-source library `NLopt`[4] for nonlinear optimization, providing easy selection between several algorithms (global, local, gradient-based). Statistical evaluation of results is performed by calculating summary statistics, sensitivities of measured data and parameters, correlation coefficients, and by estimating parameter confidence intervals using Monte Carlo simulations.

GEMSFITS codes can import, manage and query extensive sets of experimental data stored in database files in the industry-wining NoSQL BSON format[5]. Due to the flexibility of NoSQL, which does not rely on a priori knowledge of the data structure, many types of experimental data can be inserted, describing various experimental properties such as (but not limited to): chemical composition of experiments, measured phase compositions (e.g. solubility data and pH), measured phase properties (e.g. density), system volume, temperature and pressure, osmotic coefficients, activities/fugacities of components, etc.

The GEMSFITS is equipped with a graphical user interface (GUI) that allows creating a project for fitting tasks, managing the experimental data base, running the fitting task, and analyzing the results. In a project, any number of fitting tasks (variants) can be created, edited (in JSON format), and stored in the database. Multiple parameters can be fitted simultaneously against selected experimental properties, along with several options for data weighting, parameter bounds and constraints, and statistical methods. Results (parameters, sensitivity data, statistics) can be stored in database, viewed and plotted on XY plots using the GUI. The practical utility of GEMSFITS will be demonstrated by examples related to fitting thermodynamic properties of Al aqueous species using experimental solubility data.

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E-mail address: dan.miron@erdw.ethz.ch

COSMO-RS as a broadly applicable tool for solublity prediction

Andreas Klamt[1,2]

[1]COSMOlogic GmbH&CoKG, Imbacher Weg 46, Leverkusen, Germany
[2]Institute of Physical and Theoretical Chemistry,University of Regensburg, Germany

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Abstract

COSMO-RS is a relatively novel method for the a priori prediction of chemical potentials, activity coefficients, solubilities and vapor pressures of almost arbitrary chemical compounds in pure liquid solvents and mixtures. In contrast to the widely used group contribution methods COSMO-RS gets the information about the intermolecular interactions from uni-molecular quantum chemical calculations on the compounds and thus it is far less dependent on experimental data. Hence COSMO-RS is an efficient alternative to group contribution methods on the one hand and to the Monte-Carlo and Molecular Dynamics simulations on the other side. Aside from a few disadvantages it has a lot of systematic advantages. The greatest strengths are the broad applicability and extrapolation power of the method, and the systematic physical insight into the mixture behaviour of the systems, which COSMO-RS opens by its sound physical basis. Thus complicated or rare compounds can be treated and differences between isomers can be resolved.

Beyond the basic features regarding activity coefficients, vapor pressures, and enthalpies of fluid systems, COSMO-RS can be applied to solid-liquid equilibria, to solubility in polymers, to ionic liquids and electrolytes, to pKa-prediction, to adsorption phenomena and physiological partitioning, reaction thermodynamics, micelle and biomembrane binding, chromatographic retention times, crystal face polarities, and many other problems of physical chemistry which have to do with liquid phase equilibria.

E-mail address: klamt@cosmologic.de

Radionuclide behaviour in a geological disposal system for nuclear waste

V. Metz, B. Kienzler, M. Altmaier, T.Rabung, H. Geckeis

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

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Abstract

Up to 390’000 t of used UO_2 fuel from the generation of electricity by nuclear fission are forecasted to accumulate worldwide until 2015 [1]. Almost 75% of this highly radioactive waste is kept in interim storage facilities, and about a quarter of the used fuel is reprocessed in order to separate Pu and U for production of mixed-oxide fuels. Consecutive to reprocessing, residual fission products and minor actinides are vitrified. Though used nuclear fuel and highly radioactive glass comprise around 99% of the total activity inventory of radioactive waste, they comprise less than 10% of the total volume of radioactive waste products. The vast majority of radioactive waste is low and medium active waste, having a specific activity $< 10^{15}$ Bq m^{-3}. There is international consensus that disposal in deep geological formations represents the safest way to isolate highly radioactive waste products from the biosphere. Geological disposal has been the preferred option for the management of highly active as well as for the management of low and medium active waste in a number of countries, among those Germany, Switzerland and the USA.

This communication is providing an overview on radionuclide behaviour in geological repository systems for nuclear waste disposal both in view of general concepts and current research activities. In particular, it addresses the role of solubility phenomena for limiting concentrations of radionuclides in groundwater in a disposal system. Transport via the groundwater pathway holds as the most relevant mechanism for a potential radionuclide release from a radioactive waste repository and migration towards the biosphere. Aqueous radionuclide concentrations in a disposal system are determined by: Preferential leaching of a fraction of radionuclides, which are insoluble in the waste matrix, dissolution of the primary waste product, complexation with groundwater constituents, the solubility of secondary solid phases, redox reactions, sorption reactions and temporarily by coupled reaction kinetics and groundwater transport. These reactions are influenced by environmental variables, especially by pH, redox conditions, ionic strength, content of organic matter and pCO_2. In safety analyses for radioactive waste disposal systems, solubility of pure solid phases and Eigencolloids usually are considered as upper limits for the radionuclide mobilization from radioactive waste. Under ’real’ conditions, those concentrations can actually be much lower. Dissolved radionuclides when transported away from the source, may experience coprecipitation with secondary phases and sorption to surfaces of solids of engineered barriers and the geomatrix.

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E-mail address: volker.metz@kit.edu

Spent nuclear fuel and related solubility phenomena in aqueous media.

Kastriot Spahiu[a,b]

[a] *SKB, Box 250, SE-10124 Stockholm, Sweden*
[b] *Chalmers University of Technology, Nuclear Chemistry, 41296 Göteborg, Sweden*

Abstract

Spent nuclear fuel dissolution tests are usually complicated experiments due to the high radiation field and the complexity of the material. Their main aim is to study the kinetics of radiation induced fuel dissolution, which is then used to estimate the release rates of the radionuclides form the fuel, i.e. the source term for a spent fuel repository. Given their long time duration (months to years), the interpretation of the analytical data concerning the test itself cannot be carried out without a detailed understanding of the solubility and speciation of the major and minor components of the spent fuel. Since uranium is by far the major component of spent fuel, it is clear that uranium chemistry is decisive for the fuel matrix dissolution behaviour. The actinide and fission product concentrations in solutions contacting spent nuclear fuel depend on intrinsic factors such as fuel structure and burn-up, as well as environmental factors, including groundwater composition where dissolved hydrogen originating from anoxic iron corrosion is a major component.

The anoxic corrosion of massive iron containers considered in most deep disposal concepts, produces large amounts of dissolved hydrogen in the groundwater. At the relatively low repository temperatures, hydrogen is expected to be inert in bulk solution. During the last decade, a large impact of dissolved hydrogen on the dissolution of the LWR or MOX fuel and $UO_2(s)$ doped with ^{233}U or ^{238}Pu has been observed. For hydrogen concentrations above a certain limit, the dissolution rates of these highly radioactive materials drop to very low values. A discussion of the results obtained with spent fuel or α-doped UO_2 in the presence of a range of hydrogen concentrations is presented.

Typical for all measurements under such conditions are the very low long term concentrations of uranium and other redox-sensitive radionuclides, such as Tc and the minor actinides. The concentrations of U are systematically lower than the values measured during $UO_2(s)$ solubility measurements carried out in the presence of strong reducing agents. The investigation of the surface of spent fuel or $UO_2(s)$ pellets doped with ^{233}U by XPS after long periods of testing shows absence of oxidation. A summary of potential mechanisms responsible for the observed behaviour will be also given, based mainly on data from studies on the interaction of water adsorbed on the surfaces of metal oxides or actinide oxides with radiation.

Aqueous radionuclide thermodynamics and ion interaction processes

Wolfgang Hummel, Tres Thoenen

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

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Abstract

Thermodynamic equilibrium constants of aqueous species are tabulated in databases for zero ionic strength, i.e. for pure water with nothing in it, not even the species the thermodynamic datum refers to. For applying these data in real aqueous systems, the tabulated equilibrium constants have to be corrected for medium effects. For very dilute systems the Debye-Hückel limiting law describes electrostatic effects between mathematical point charges. For dilute systems the extended Debye-Hückel equation addresses the fact that ions are not point charges. For ground waters with moderate salt concentrations deviations from the Debye-Hückel behaviour can be accounted for by introducing ion association (weak complexes) in the aqueous speciation model. A mathematically correct example will be shown. If the salt concentration increases beyond 0.1 $mol \cdot kg^{-1}$ we have to consider specific ion interactions, for example using the Specific ion Interaction Theory (SIT) or the Pitzer formalism.

There are three principal sources of ion interaction coefficients: (1) Derivations from osmotic coefficients (or mean activity data) which usually come from isopiestic measurements of soluble salts. (2) Derivations from the variation of conditional equilibrium constants measured at different concentrations of background electrolytes. (3) Estimates based on some chemical systematics.

Ion interaction approaches do not need weak ion association in their models but have to consider strong complexes explicitly. There is no agreement about the threshold between weak and strong complexes, and this lack of agreement "spoil" all available ion interaction coefficient sets.

As a worked example we will look at the complexation of U(VI) with edta (ethylenediamine tetraacetate) in NaCl solution. SIT regression analyses of conditional equilibrium constants can be done either by assuming that interactions between UO_2^{2+} and Cl^- ions in solution are all included in the SIT parameters or by explicitly considering U(VI) – chloride complexation. Both approaches fit the experimental data equally well, but the resulting equilibrium constants at zero ionic strength and the derived SIT parameters are different.

Aiming at internal consistency we would have to derive two databases for radionuclide complexes applicable in NaCl solutions: One with explicit inclusion of radionuclide – chloride complexes and another one including all chloride interaction in SIT parameters. In agreement with the late Volker Neck we advocate to go for the latter one: Use the least number of adjustable parameters in your thermodynamic model.

In the course of updating our PSI/Nagra database we scrutinized the origin and completeness of reported SIT parameters. In the case of $NaClO_4$ media a considerable number of experimentally derived or estimated ion interaction coefficients are available. However, for NaCl media a large number of missing data was detected. In both cases, many values recommended in the reports turned out to be estimated.

We used the new but smaller set of experimentally derived ion interaction coefficients to revise our correlations of SIT parameters with charge. The correlations got worse but did not vanish. However, in the case of NaCl media this correlation is still "contaminated" with the inconsistent treatment of chloride interactions in the different reports. This problem cannot be resolved without a complete re-evaluation of experimental data. Nevertheless, we still can use the correlations for rough estimates of missing SIT parameters.

E-mail address: wolfgang.hummel@psi.ch

Speciation of Actinides by Time-resolved Laser Fluorescence Spectroscopy

Petra J. Panak

Institute of Physical Chemistry, University of Heidelberg, 69120 Heidelberg, Germany

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Abstract

Spectroscopic actinide speciation, providing fundamental information on processes on a molecular scale, is essential for performance assessment of nuclear waste repositories and useful for development of partitioning strategies. Time-resolved laser fluorescence spectroscopy (TRLFS) is a sensitive speciation technique, which allows actinide characterization and quantification without disturbing the chemical equilibrium. Cm(III) has excellent fluorescence properties and thus can be used as a representative for the trivalent actinides in speciation studies down to the nanomolar range. TRLFS provides information on the structure of An(III) complexes and can be applied not only to solutions but also to solids and suspensions. In this presentation examples of the application of TRLFS for actinide speciation in research issues related to nuclear waste disposal and partitioning are given:

a) In order to model the aqueous speciation of actinides in aquatic systems, fundamental knowledge of the participating chemical reactions and the corresponding thermodynamic data are needed. In the past few years considerable progress in establishing a thermodynamic database for lanthanides and actinides has been achieved. However, most of the available data are restricted to temperatures near 20°C. Depending on the disposed waste and the surrounding technical and geological barrier, the temperature in the direct vicinity of the repository can reach up to 200°C. Therefore, it is necessary to determine stability constants and thermodynamic data at elevated temperatures. A high temperature and high pressure cell for TRLFS has been developed and applied to study complexation reactions with various organic and inorganic ligands in the temperature range from 20-200°C. The results show that TRLFS is a powerful method to obtain thermodynamic data at elevated temperatures crucial for a reliable description of the migration behaviour of trivalent actinides (An(III)) in the near field of a nuclear waste repository.

b) Partitioning may be used to isolate long-lived radionuclides from nuclear fuel reprocessing waste for subsequent transmutation to shorter lived or stable nuclides, or for their conditioning and immobilization in special matrices for disposal. The separation of trivalent actinides (An(III)), namely Am(III) and Cm(III), from lanthanides (Ln(III)) is a key step in the partitioning & transmutation (P&T) strategy. The chemical properties and the ionic radii of An(III) and Ln(III) are comparable, rendering high demands on the selectivity of the extraction ligand in liquid/liquid extraction processes. Various soft N-donor ligands have been developed, which extract An(III) selectively over Ln(III) from nitric acid solutions into the organic phase with separation factors for Am(III) or Cm(III) vs. Eu(III) of > 100. Our research focuses on attempts to understand the underlying reason for the partitioning ligand selectivity. TRLFS is used for determination of coordination structures and thermodynamic data for Cm(III) complexed with various N-donor ligands and comparison to those of their Eu(III) counterparts. The results are of particular importance to optimize partitioning ligand design and, hence, extraction performance.

E-mail address: petra.panak@kit.edu

Redox processes and aquatic chemistry in the safety case of deep geological repositories of radioactive wastes

L. Duro, M. Grivé and J. Molinero

Amphos 21, Passeig Garcia i Faria, 49-51, 1-1a, 08019 Barcelona, Spain

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Abstract

The Safety Case is defined as the collection of scientific, technical, administrative and managerial arguments and evidences in support of the safety of a disposal facility, covering, among other subjects, the suitability of the site and the design, construction and operation of the facility, the assessment of radiation risks and assurance of the adequacy and quality of all of the safety related work associated with the disposal facility. *Safety Assessment*, an integral part of the Safety Case, is driven by a systematic assessment of radiation hazards. Both of them, Safety Case and Safety Assessment of a geological disposal facility of high level radioactive waste are continuously evolving and being fed by the different research and technologic activities developed at very different levels for all the subsystems conforming the scheme of the repository. In fact, the safety case evolves step by step and the scientific understanding of the disposal system and of the facility is progressively improved. As new findings appear, focus of research activities must be reoriented or reinforced in specific issues of concern. Redox processes, and their influence on solubility and dissolution phenomena, as well as the understanding of aqueous complexation processes influencing solubility become main issues to study when developing a Safety Case and when assessing the performance of a given geological disposal system. In this work, an overview of the influence of different studies developed in the last years on the description of redox and solubility processes, and how they have been implemented in conceptual and numerical models is presented, with focus on specific cases. The cases include both experimental studies as well as hydrogeochemical modelling that have been (and are) applied in support of safety and performance assessment.

E-mail address: lara.duro@amphos21.com

Applications of Molten Salts in Nuclear Technology

Thomas Fanghänel, Ondrej Beneš, Jean-Paul Glatz, Rudy Konings,
Rikard Malmbeck, Pavel Souček

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

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Abstract

Molten salts have interesting applications in nuclear technology because they have a high resistance to radiation, possess of high thermal stability and have good retention capacity of volatile fission products. For these reasons they are studied as solvents for separation processes, and as fuel and/or coolant in innovative reactors.

Molten salt separation techniques are principally studied in the frame of future advanced nuclear energy systems that are characterised by effective fuel utilization for sustainability and waste minimization through recycling and transmutation ("burning") of actinides in dedicated reactors [1]. The fuels used in the advanced reactor systems are likely to be significantly different from the present commercial fuels and their processing by hydrometallurgical methods might not be suitable. Therefore, different pyrochemical separation techniques using high temperature and radiation resistant molten chloride or fluorides salts solvents are developed [2]. The main pyrochemical processes are based on electrochemical methods (electrolysis or electrorefining) and reductive extraction. Apart from basic research on the electrochemical methods for nuclear fuel processing, the technology has been tested at JRC-ITU in the METAPHIX project [3], which is an experimental demonstration of a closed metal fuel cycle, and further includes fabrication, irradiation at the Phenix reactor, post-irradiation examination.

In the molten salt reactor (MSR) a liquid mixture of metal fluorides is used as a fuel and coolant. The MSR belongs to the group of six reactor concepts considered within the GenIV international forum and can be used to burn higher actinides or as a breeder based on the ^{232}Th/^{233}U closed fuel cycle. To identify the optimal composition of the fuel salt and to perform the safety assessment of the reactor a fundamental knowledge of the physico-chemical properties of the molten fluoride salts must developed. In this context systematic experimental studies of binary and ternary salt mixtures are ongoing at JRC-ITU focusing on key properties such as heat capacity, solubility of actinides in the fuel solvent, melting temperature, phase diagram data and vapour pressure. The results from these measurements are used to establish a comprehensive thermodynamic database which is an essential tool to predict the chemical behaviour of the fuel salt during normal operation and accident conditions.

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E-mail address: Thomas.FANGHAENEL@ec.europa.eu

Liquid phase behaviour in systems containing ionic liquids: can “old-fashioned” experiments enable us to understand their properties and structure?

Magdalena Bendová

E. Hála Laboratory of Separation Processes, Institute of Chemical Process Fundamentals AS CR, v. v. i., Rozvojová 135/1,
165 02 Prague 6, Czech Republic

Dedicated to the memory of the late prof. Eduard Hála (1919–1989).

Abstract

Advanced spectroscopy methods and molecular simulation modelling enable us to see as deep as the molecular-level structure of pure compounds and mixtures. Because bulk thermophysical and thermodynamic properties of mixtures are influenced by those underlying structural effects, it is often possible to estimate them from macroscopic data based on what is known about microscopic structure. For instance, molecular simulation studies have shown that nano-segregated clusters of polar and non-polar domains tend to form in pure ionic liquids and their solutions with molecular compounds [1, 2]. This, along with whether the ionic liquid and the molecular solvent molecules form H-bonds or not or whether they associate or self-associate may be used to judge on the relationships between structure and liquid phase behavior [3].

Is therefore the “old-fashioned” experiment dead? A judicious symbiosis between macroscopic experiments, spectroscopy, and molecular modelling should be the answer. To demonstrate the possibilities and limits of this approach, examples of liquid phase behavior data and other properties obtained for systems containing ionic liquids will be used in the present contribution.

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E-mail address: bendova@icpf.cas.cz

An IR and computational study of the hydrogen bonding to uracil in aqueous DMSO mixtures

Earle Waghorne, Maryam Mohammadpoor, Linda Sherry, Finn Milton-Purcell

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

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Abstract

Some years ago the Symons group [1] developed a simple infrared spectroscopic technique for studying hydrogen bonding to functional groups of molecules in solution. Briefly, in an aprotic solvent no hydrogen bonds are formed to basic chromophores; when a protic solvent is added hydrogen bonds are formed and, in good cases, separate infrared peaks are produced for each hydrogen bonded species formed. In effect the technique directly determines the speciation diagram and the number of hydrogen bonds formed at a chromophore.

The technique has been applied to a range of compounds with single basic chromophores but not to the nucleic acid bases, despite the importance of hydrogen bonding in their functioning.

Partly this is because the spectra of uracils are complicated by the presence of the two C=O moieties, giving rise to two strong absorptions, both of wich are affected by hydrogen bonding to either C=O oxygen. To clarify the interpretation of the infrared spectra, the study was augmented by a series of quantum mechanical calculations.

The present paper presents an infrared study of the C=O chromophores of uracil and *N,N*-dimethyuracil in mixtures of dimethylsulfoxide, DMSO, and D_2O.

The calculations indicate that the positions of each of the C=O based absorptions is sensitive to the numbers of waters hydrogen bonded to the carbony oxygens ($n_{\mathrm{W(01)}}$ and $n_{\mathrm{W(O11)}}$) and follow the general equation:

$$\omega = \omega^{\mathrm{o}} + an_{\mathrm{W(O1)}} + bn_{\mathrm{W(O11)}}$$

and this is consistent with the variations in the peak positions found in the experimental spactra.

The results show that, in water, the principal species of uracil (ca 70 %) is one in which each C=O oxygen atom is hydrogen bonded to two water molecules, in agreement with the results of a recent molecular dynamics simulation [2]. It is also clear that hydrogen bonding to the C=O oxygens of *N,N*-dimethyluracil is weaker than to uracil.

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E-mail address: earle.waghorne@ucd.ie

Solubility and phase processes in water – organic multicomponent systems with non-equilibrium chemical reactions

Alexander Toikka, Artemiy Samarov, Nikita Tsvetov, Irina Letyanina

Department of Chemical Thermodynamics and Kinetics, Institute of Chemistry, Saint-Petersburg State University,
Universitetskiy prospect 26, Peterhof, Saint-Petersburg, 198504, Russia

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Abstract

The simultaneous phase and chemical equilibria are the objects of numerous investigations of recent decades. Such researches are of both basic and applied importance, e.g. for the design of coupled synthesis and separation processes. The studies of systems in partly nonequilibrium states (e.g. with nonequilibrium chemical reaction) are more limited in comparison with traditional works on equilibrium data. Nevertheless the study of heterogeneous systems in chemically nonequilibrium states gives the additional opportunities for the chemical engineering process design. In these cases one should take into account not only thermodynamic conditions for coupled processes but also some elements of chemical kinetics. In more complex case of miscibility gap the differences of reactions rates in coexisting phases and mass-transfer between phases should be considered. The aim of the lecture is to present some recent results of our works on the study of solubility and related thermodynamic properties in multicomponent water – organic systems with chemical reactions.

For the sake of simplicity the results of theoretical study is presented for the case of ternary systems with limited solubility. Thermodynamic consideration of chemically nonequilibrium states includes the analysis of the dependence of affinity on reaction extent and composition. The change of the affinity on binodal curves is determined by the run of chemical equilibrium curve, tie-lines and stoichiometric lines dispositions in composition triangle. The conditions of the extremum of the affinity and disposition of chemical equilibrium curves in composition triangle of heterogeneous system are discussed.

The main object of our experimental study are nonequilibrium chemical reactions accompanied by liquid phase splitting in a few water–organic quaternary systems. We present a new data on solubility, phase properties and heterogeneous kinetic behavior for the systems with ester synthesis reactions. The case of reaction passing through heterogeneous regions is considered. Experimental results were compared with calculations using UNIFAC and NRTL models. We also present the experimental data on enthalpies of mixing (H_m) in reaction media. The determination H_m in the case of chemical interaction of components is a special problem: one should separate H_m from the heat of reaction. The thermochemical experiments were carried out with the use of equipment of Resource Center of Thermal Analysis and Calorimetry of SPbSU (C80 calorimeter with membrane mixing cells by Setaram Instrumentation).

Some general problems of the study of systems with limited solubility and chemical interactions would be discussed on the base of our results and literature data.

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E-mail address: alexander.toikka@chem.spbu.ru

Hydrotropic solubilisation of β-pinene: Phase behavior and 2D NMR DOSY investigation of the effect of linalool.

Thomas Lukowicz, Valérie Molinier, Véronique Nardello-Rataj, Jean-Marie Aubry*

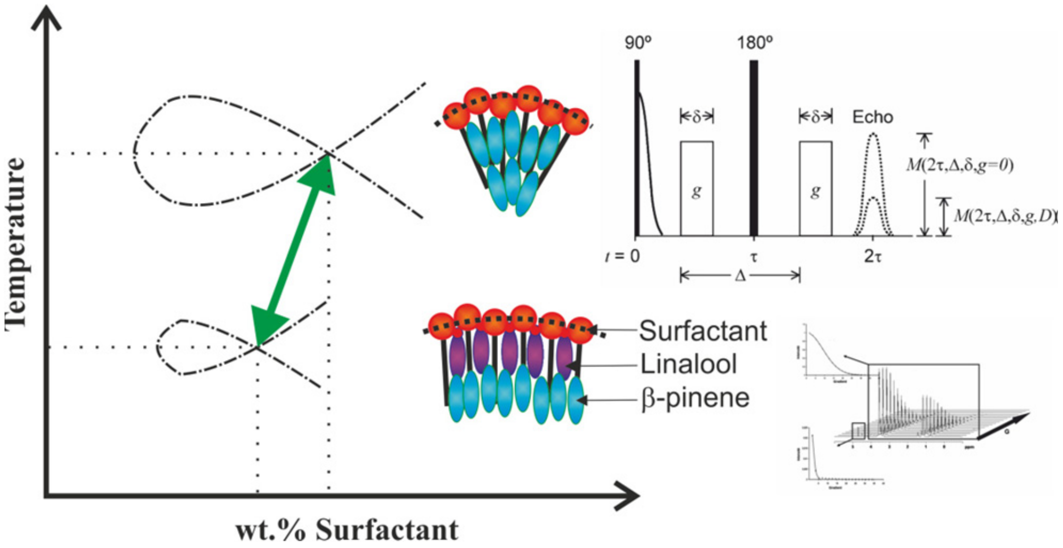
Université Lille 1 and ENSCL, EA 4478 Chimie Moléculaire et Formulation, Equipe « Oxydation et Physicochimie de la Formulation »,
F-59655 Villeneuve d'Ascq, France.

Abstract

The solubilisation of polar oils in aqueous micellar solution is in the focus of recent research [1]. Especially for water-based perfumery it is of greater interest, since fragrances do not mix with water due to their hydrophobic character. Furthermore it is desired to use as little surfactant as possible to solubilise as much polar oil as possible.

In this work we want to show how the mixing of polar oils can result in an increasing efficiency of the surfactant to solubilise these oils. The terpene β-pinene and the more polar terpenoid linalool were used to construct Fish Cut diagrams with tetraethylene glycol monohexylether (C_6E_4) as a solubilizing agent. Unlike non-polar oils, β-pinene and linalool are able to penetrate into the interface. Especially linalool with its OH-group has a relatively high amphiphilicity and acts as a co-surfactant, which alters the curvature of the micelle [1,2].

These alterations have an effect on the diffusion characteristics of the aggregates which were investigated with 2-dimensional diffusion ordered H-NMR spectroscopy (2D-DOSY NMR) [2-3]. Therefore measurements of an aqueous C_6E_4 solution were performed in order to determine the diffusion coefficient and the micelle size. Furthermore, the effect of β-pinene and linalool on these parameters was investigated.



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E-mail address: lukowicz.thomas@googlemail.com

Flavonoids solubility in organic solvents: molecular modelling, thermodynamics and physico-chemical investigations

Latifa Chebil,[1] Claire Gaiani,[1] Mohamed Bouroukba,[2] François Dehez,[3]
Catherine Humeau,[1] Jean-Marc Engasser,[1] Mohamed Ghoul[1]

[1]Université de Lorraine, ENSAIA - LIBio (Laboratoire d'ingénierie des biomolécules),
2 avenue de la forêt de Haye, 54500 Vandœuvre-lès-Nancy, France.
[2]Université de Lorraine, ENSIC - LRGP (Laboratoire Réaction et Génie des Procédés),
1 rue Grandville, B.P. 20451, 54001 Nancy, France
[3]Université de Lorraine, Equipe de Dynamique des Assemblages Membranaires, UMR CNRS-UHP N° 7565,
BP 70239, 54506 Vandœuvre-lès-Nancy, France.

Abstract

Flavonoids are the largest class of phenolic secondary metabolites in plants. They are powerful antioxidants and have been reported to possess a wide range of biological effects[1]. However, the solubility of these molecules in different media (water, organic solvent, hydrophobic media) is a complex and important process. It is a key factor in extraction, formulation and biocatalysis processes of flavonoids. We reported here experimental and molecular modelling approach of flavonoid solubility. Experimentally, in acetone and *tert*-amyl alcohol, the solubilities at 50°C of quercetin, isoquercitrin and rutin, were found in the range of 20 to 40 g/L, much higher than their solubilities in water, which do not exceed a few g/L, or in acetonitrile (0.3-1.7 g/L)[2]. To explain the high solubility values of flavonoids in acetone and *tert*-amyl alcohol, we investigated molecular dynamics simulations and free energy perturbation (FEP) methodology, to predict the relative free energies of solvation of quercetin in a variety of solvents, and thermodynamic measurements. The computed free energies of solvation (ΔG_{solv}) are consistent with the experimental solubility scale for quercetin, i.e. water < acetonitrile < *tert*-amyl alcohol ≈ acetone[3]. Also, the measured enthalpies of dissolution (ΔH_{diss}) and mixing (ΔH_{mix}), are consistent with the experimental solubility scale for quercetin, isoquercitrin and rutin, i.e. rutin/*tert*-amyl alcohol < isoquercitrin/*tert*-amyl alcohol < quercetin/*tert*-amyl alcohol < quercetin/acetonitrile, with values ranging from ca. 12 to 180 J/g and -123 to 43 J/g, respectively[4]. Otherwise, quercetin in *tert*-amyl alcohol showed an unusual behaviour of the amount dissolved over time. High concentrations of dissolved quercetin were measured at the beginning of the experiment. The maximum concentration was followed by a decrease later on in time until the saturation concentration was obtained. Microscopic observations and particle size measurement showed an increase of quercetin particles size, in *tert*-amyl alcohol, throughout the dissolution process (0.4 and 8 µm at 5 min, after 68 min of dissolution 14-60 µm). This surprising behaviour, in contrast to the experience in common dissolution experiments (quercetin, isoquercitrin and rutin in acetonitrile, isoquercitrin and rutin in *tert*-amyl alcohol), has never been observed for flavonoids and is called kinetic size effect.

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E-mail address: Latifa.chebil@univ-lorraine.fr

New strategy for the solubility determination of phenolic acids

Emilia Furia, Antonio Tagarelli, Giovanni Sindona

Department of Chemistry and Chemical Technologies, University of Calabria, Arcavacata di Rende (CS), I-87036, Italy

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Abstract

The tendency of each phenolic acid to be solubilized, transferred, or diffused into a given solvent is governed by thermodynamics. It was reported in the literature that the low solubilities in water of some solutes can be modified by the presence of cosolutes such as salts or by increasing the temperature [1-3]. Two phenomena related to solubility changes caused by the presence of cosolutes can be observed: salting-in and salting-out effects.

In this work the solubility of vanillic, gallic, syringic, coumaric, caffeic and ferulic acids in aqueous solutions of various concentrations in sodium chloride was determined. Saturated phenolic acids solutions were prepared with a leaching apparatus suitable to prevent solid particles from coming into contact with the magnetic stirrer. Preliminary measurements showed an increase of solubility over periods of weeks when the solid was in mechanical contact with the stirrer because the solid was transformed into a phase made of smaller particles. To avoid grinding by the stirrer, solid phenolic acids were wrapped up in a highly retentive filter paper bag. These in turn were kept in glass cylinders containing sodium chloride solution at pre-established ionic strength values (*i.e.* I=0.16 mol/dm^3) and in pure water while continuously stirring with a magnetic bar. The cylinders were then placed in a thermostatic water bath at (310.15±0.05) K, and the phenolic acids concentration was monitored over time, until it reached a constant value, which usually occurred in about (2 to 3) days.

Finally a novel, simple, rapid and selective approach in the assay of these phenolic acids by solid phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC–MS) is used [4]. A preliminary derivatization with ethyl chloroformate/ethanol was used and the corresponding derivatives were then extracted by SPME in immersion mode.

Results showed a salting-out effect on the solubility of the tested phenolic acids.

This work is a continuous effort concerning the salt addition effect on organic compounds solubility [5-8].

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E-mail address: emilia.furia@unical.it

Search of co-solvents of poorly water-soluble bioactive compounds in natural products on the basis of the solubility measurements

Hiroyuki Matsuda,[1] Mami Ozawa,[1] Kiyofumi Kurihara,[1] Katsumi Tochigi,[1]
Kazuo Tomono[2]

[1]Department of Materials and Applied Chemistry, Nihon University, 1-18-14 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan
[2]College of Pharmacy, Nihon University, 7-7-1 Narashinodai, Funabashi, Funabashi, Chiba, Japan

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Abstract

We have studied an enhancement of solubilities of poorly water-soluble pharmaceutical compounds by adding co-solvents, e.g., ethanol, polyethylene glycol (PEG), surfactant, and cyclodextrin (CD) or its derivatives [1-2]. The object of this study is to search a suitable co-solvent of poorly water-soluble bioactive compounds in natural products on the basis of the solubility measurements. In this study, curcumin (diferuloymethane), the Indian solid gold, the major active component of turmetic, was selected as a model bioactive compound. Curcumin is used as a spice in curry and as a coloring agent in yellow mustards, cosmetics, and pharmaceuticals [3]. Recently, it has attracted great interest because of its antioxidant, anti-inflammatory, and potential cancer chemopreventive activities [4]. However, the major problem with curcumin is its extremely low solubility in aqueous solution and poor bioavailability. If addition of a suitable co-solvent makes an enhancement of solubilities of curcumin, it would be useful for the development of drug or functional food which an efficient systemic absorption is available.

In this work, β-CD and three β-CD derivatives, e.g., 2-hydroxypropyl- (2-HP-), sulfobutyl ether (SBE-), and methyl- (M-) β-CDs, were investigated as a co-solvent. The solubilities of curcumin in water + CD mixed solvents, and a suitable co-solvent for an enhancement of the solubilities in curcumin was examined.

The solubilities of curcumin in water + CD mixed solvents at 298.15 K were determined using high-performance liquid chromatography (HPLC). The experimental solubilities increased with increasing of CDs. Maximum enhancements of the solubility in curcumin could be achieved by M-β-CD, and 250 times in the mole fraction basis of the solubility enhancement could be obtained, compared to the solubility in pure water. SBE-β-CD and β-CD also gave the solubility enhancements 167 and 143 times, respectively. In addition, the solubilization power was evaluated using a log-linear model. The order of the solubilization power was M-β-CD > SBE-β-CD > 2-HE-β-CD. From these results, it can be concluded that chemically modified CD derivatives are more suitable co-solvents for an enhancement of the solubilities of curcumin, while β-CD gives a relatively high solubilization power.

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E-mail address: matsuda.hiroyuki@nihon-u.ac.jp

Actinide Chemistry in Chloride Brine Solutions

Wolfgang Runde

SPO-SC, Los Alamos National Laboratory

Abstract

Although hydroxide and carbonate are the most important inorganic ligands in natural environments, chloride has been critical for nuclear waste management in geologic salt formations as well as separation processes. Despite the weak interaction of chloride with the actinide ions, chloride ions can impact the chemistry of actinides in solution and solid state in multiple ways. Examples are the impact on solubility and speciation, intercalation in solid state materials or the radiolytic formation of oxidizing species. We investigated the actinyl(III,V,VI) chloride complexation by using UV-vis absorbance, Raman and FTIR spectroscopies and determined formation constants of $AnO_2Cl_n^{2-n}$ complexes where n = 0-3. In concentrated NaCl solution three complexes can be present while higher chloride concentration (i.e. concentrated LiCl) is needed to form the limiting An(VI) chloro species, $AnO_2Cl_4^{2-}$. The stabilities of the U(VI) chloro complexes are compared to those of other hexavalent actinides, e.g. those of Pu(VI). We will discuss the impact of chloride complexation on the hydrolysis and carbonate complexation of the actinyl(III, V,VI) ions, as well as radiolytic effects in concentrated chloride solutions and their effect on actinide oxidation state stabilities. The impact of chloride on the solubility of actinides will be illustrated with Np(V) and U(VI) in carbonate-containing solutions.

E-mail address: runde@lanl.gov

Solubility and the periodic table of elements

Cezary Guminski

retired from: Department of Chemistry, University of Warsaw, Pasteura 1, 02093 Warsaw, Poland

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Abstract

A fundamentally important matter in teaching inorganic chemistry is to convince students that changes of various properties of elements and their compounds (well then a solubility) are strongly connected with the position of these elements in the periodic table. This presenter was co-author of 8 volumes for the IUPAC-NIST Solubility Data Series of various type of systems [1-8] and observed some general tendencies in the changes of solubilities of elements and their compounds when the corresponding data were arrayed according to the increasing atomic number of elements.

In case of the metallic systems, the solubilities of low melting metals in mercury as well as in liquid alkali metals are generally high whereas the solubilities of high melting metals and nonmetals are rather low. These solubility values change with the atomic numbers in a quite similar way as the temperatures and energies of melting or boiling of the metals. In alkali metals with the transition metals dissolved in, some side reactions with nonmetallic impurities are very important to be taken into account.

The solubilities of intermetallic compounds in mercury depended reciprocally on the energies of formation of these intermetallics in the binary alloys and depended also on the dissolution energies of the component metals in mercury.

Concerning the several selected systems of salts in water, it may be observed that the known solubilities of metal halates showed well defined periodical changes. The arrayed solubility data of rare earth metal halides in water displayed quite smooth changes with the increasing atomic number when the saturating solid phases were isomorphic.

These observations may be useful in a prediction of solubility for experimentally unknown systems.

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E-mail address: cegie@chem.uw.edu.pl

Modelling actinide solubilities in alkaline to hyperalkaline solutions: Part two, solubility of Pu(IV) in NaOH solutions[A]

Yongliang Xiong, Christi D. Leigh

Repository Performance Dept. 6212, Sandia National Laboratories[B], 4100 National Parks Highway, Carlsbad, NM 8822, USA

Abstract

Accurate knowledge of actinide speciation and solubilities in highly alkaline solutions is important to nuclear waste management. First, in the tank wastes such as those at Savannah River site and Hanford site, the solutions contain high concentrations of bases [1-2]. Second, the solutions in equilibrium with cements in geological repositories would also be highly alkaline with concentrations of OH^- in the order of hundreds of milli-molars [3]. Accurate predictions of actinide solubilities in these highly alkaline solutions with ionic strengths above 3.5 m require a thermodynamic model applicable to high ionic strengths with high base concentrations. The well regarded NEA series on chemical thermodynamics of actinides [4] are based on the specific ion interaction theory (SIT) activity coefficient model for evaluation, which is valid to an ionic strength of ~3.5 m. Furthermore, the speciation scheme in the NEA series does not extend to the highly alkaline region. Therefore, it is not suitable for modeling actinide solubilities in highly alkaline and highly concentrated solutions.

In an attempt to systematically assess the speciation and solubility of actinides in alkaline to hyperalkaline solutions, the studies at Sandia National Laboratories (SNL) have evaluated the stability constant of $Am(OH)_4^-$ based on the solubility data in KOH solutions up to ~12 m by using the Pitzer equations [5]. This species is demonstrated to be important in hyperalkaline solutions.

In this work, solubility data of Pu(IV) in NaOH solutions from the literature are modelled to obtain the thermodynamic parameters by using the Pitzer equations. The platform for the modeling is the computer program EQ3/6 Version 8.0a [6-7].

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E-mail address: yxiong@sandia.gov

Solubility of some transition metals halides in organic and mixed aqua-organic solvents

Mikhail Skripkin,[1] Artyom Gorbunov,[1] Nikolai Tcyrulnikov,[1] Nikita Bogachev,[1] Anastasiia Tikhomirova[1,2]

[1]Institute of Chemistry, Saint-Petersburg State University, Universitetsky prospect, 26, 198504, Saint-Petersburg, RUSSIA
[2]Bowling Green State University, Center for Photochemical Sciences, 1001 E. Wooster, 43403, Bowling Green, Oh, US

Abstract

Solution – solid phase equilibria and their dependence on the properties of solutes and solvents have been one of the principal problems of Solution Chemistry for a long time. A lot of systems have been studied experimentally, and some theoretical approaches have been developed. Nevertheless, the major part of the existing data concerns the aqueous solutions only; as to the solubility of electrolytes in organic and especially in mixed aqua-organic solutions, these data are quite limited. In this communication some regularities of transition metals halides solubility in organic and mixed aqua-organic solvents will be discussed.

The choice of oxygen-donating organic solvents (dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, 1,4-dioxane) enables us to avoid the effect of the specifics of donor atom. At the same time, solvent properties such as dielectric permittivity, donor number and hardness/softness (Marcus's scale [1] was used) vary widely. As to the metal ions, the stability constants of halide complexes differ significantly that allows us to reveal the effect of ionic association in liquid phase on the liquid- solid equilibria.

Dielectric permittivity and softness of solvent were considered to be the principal parameters that determine the solubility of salts. No correlation between any of these parameters taken alone and the concentrations of saturated solutions can be established even at the qualitative level. But the use of their combination can give far better results. In this work the simple empirical equation has been suggested to describe the dependence of salt solubility in individual solvent on dielectric permittivity of solvent and softness parameter in Marcus scale. The contribution of these parameters varies dependent on the salt's nature according to the theoretical prediction. This approach was tested for several salts; the solubility in some other oxygen-donor solvents was predicted and the experimental data obtained later were in rather good agreement with these predictions.

Theory of hard and soft acids and basis was also successfully applied to the analysis of solubility isotherms and regularities of solid compounds crystallization. Some correlations between softness of solutes and solvents and, on the one hand, formation of stable associates in liquid phase, on the other hand, the shape of solubility isotherms and positions of the eutoinic points were established. The reasons of coordination disproportion and formation of regions of immiscibility have been proposed. Effect of the softness of solute and solvent on the kind of solid compounds crystallizing from mixed aqua-organic solutions was revealed.

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E-mail address: skripkin1965@yandex.ru

A comparative study of uranium and plutonium transfer during liquid-liquid extraction

Anne Lélias-Vanderperre, Romain Berlemont, Manuel Miguirditchian

CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, SMCS/LEPS, Bagnols-sur-Cèze, F-30207, France

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Abstract

In the frame of the development of Generation IV reactors, new liquid-liquid extraction processes are under development for the reprocessing of spent nuclear fuels. Thermodynamic and kinetic experimental data are necessary for the modeling and the simulation of the extraction operations in these processes.

This paper concerns the acquisition of mass transfer coefficients of actinides between nitric acid and a monoamide-based solvent. Because of the existence of many kinetic methods[1], this study was focused on a constant interfacial area technique, the single drop technique, to determine the mass transfer kinetics of uranium(VI) and plutonium(IV) upon extraction by monoamides from an aqueous nitric solution. This method relies on a liquid drop (organic or aqueous phase) that runs into a continuous phase through the column. During the drop course, the mass transfer occurs and the drop analysis leads to the determination of the kinetic constants.

The influence of temperature, solute concentration, interfacial area (drop size), viscosity of the organic phase and emulsion nature (continuous aqueous or organic phase) on the kinetics of uranium and plutonium extraction has been studied. The results have been exploited to determine either the chemistry or the diffusion process controls the kinetic.

These data are compared with results obtained in similar conditions with TBP solvent currently used in the PUREX process in order to estimate the difference of kinetics between these two solvents.

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E-mail address: anne.lelias@cea.fr

Thorium as an analog for actinide(IV) solubility in brine

Donald Reed, Michael Richmann, Danielle Cleveland, Marian Borkowski

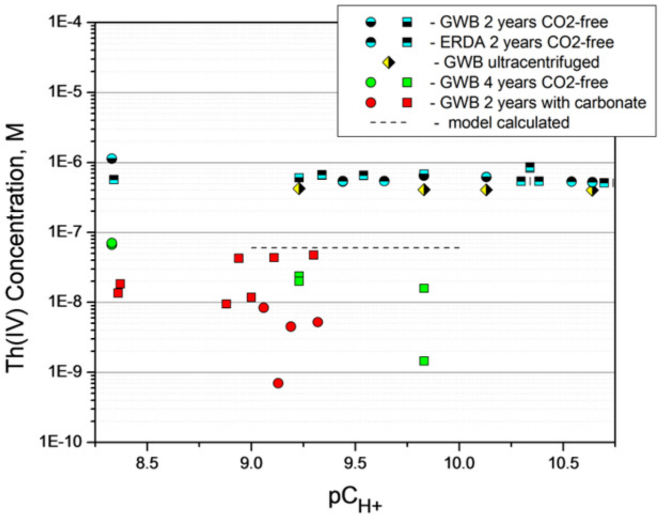
Repository Science and Operations, Los Alamos National Laboratory, 1400 University Ave, Carlsbad NM, USA

Abstract

Thorium is widely used as a redox-invariant analog for An(IV) species in repository safety case considerations. This application was recently evaluated for the Waste Isolation Pilot Plant (WIPP) project in a series of long-term studies in simulated brine as a function of pH and time [1]. There remain positive and negative aspects of the thorium analog and an assessment of these in the context of the WIPP PA application will be presented.

The WIPP-specific thorium solubility results obtained are summarized in Figure 1. After 2 years of equilibration in carbonate-free brine, the measured solubility of thorium was 6-7×10^{-7} M and was essentially independent of pH and brine composition over the 6.5 to 11.5 pC_{H+} range investigated (blue/black points). Sequential filtration to ~ 10 nm pore size had little effect on the measured concentration. Subsequent ultracentrifugation up to 1,000,000 g resulted in up to a 40% colloidal fraction, indicating that there was relatively little intrinsic colloid formation. The steady-state thorium concentrations we measured are consistent with literature reports for simplified brine systems [2] but show a significantly lower extent of aggregation to form intrinsic colloids.

Figure 1. The concentrations of thorium measured in WIPP simulated brines both ERDA-6 and GWB) as a function of time, filtration, and the presence of carbonate (circles: oversaturation, squares: undersaturation). Although high, but meta-stable, concentrations were initially present, in time the measured concentrations decreased and are conservatively below the WIPP model-predicted values.



After an additional 2 years of equilibration in the undersaturation experiments, which are most relevant to the WIPP, the average thorium concentration was 2×10^{-8} M and continued to decrease at $pC_{H+} > 9$. At the expected WIPP repository pC_{H+} (~ 9.5), and in the presence of carbonate, the thorium concentration in GWB was 2×10^{-8} M or lower. This concentration trend suggests that the mixed hydroxy-carbonato complexes do not play a significant role in the thorium solubility at $pC_{H+} > 9$. Throughout these experiments, significant dis-equilibrium persisted for relatively long times and nano-filterable species were observed under most conditions making rigorous interpretation of the data in terms of solubility difficult. Overall, these difficulties lead to conservatively high estimates of An(IV) solubility making this a good approach from a regulatory point of view.

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E-mail address: dreed@lanl.gov

The role of sulphur speciation in abiogenic sulphate reduction

Laurent Truche,[1] Elena Bazarkina,[1,2] Guillaume Barré,[1] Emilie Thomassot,[3]
Gilles Berger,[4] Jean Dubessy[1]

[1] *Université de Lorraine; GeoRessources, BP 70239, F-54506 Vandœuvre-lès-Nancy, France*
[2] *RAS; IGEM; Staromonetny per. 35, 119017 Moscow, Russia*
[3] *CNRS, CRPG, 15 rue Notre Dame des Pauvres, Vandœuvre-lès-Nancy, F-54501 France*
[4] *CNRS; IRAP; 14 avenue Edouard Belin, 31400 Toulouse, France*

Abstract

Thermochemical sulphate reduction (TSR) plays a crucial role in the global sulphur cycle in the Earth's crust, and may affect current and past sulphur isotopic records. The occurrences and consequences of TSR have been documented[1] over the past fifty years in numerous geological contexts worldwide, at T ranging from 100°C to more than 400°C. However, the poor constraints on the reaction mechanisms hamper the extrapolation of experimental reaction rates measured at high temperature (above 200°C) towards lower temperatures, and make it difficult to interpret the sulphur isotopic fractionation recorded in natural samples. Several authors[2,3,4,5] have suggested that the auto-catalytic effect of H_2S on TSR is due to its reaction with sulphate to produce elemental sulphur or various intermediate sulphur valence species, which in turn react with the reducing agent to produce H_2S, or act as a bridge for the transfer of electrons from S^{6+} to S^{2-}. Observed reaction rates are extrapolated to lower temperatures relevant to geologic conditions *via* an Arrhenius law, assuming that the reaction mechanisms remain unchanged. This assumption is particularly problematic because the speciation of sulphur species involved in the reaction path strongly depends on pH and T[6].

Based on *in-situ* Raman spectroscopy measurements, we show that the trisulphur ion S_3^- is the dominant intermediate sulphur valence species involved in abiogenic sulphate reduction processes initiated by H_2S, over a wide range of temperature (100-350°C) and solution compositions, whatever the electron donor considered. The in-situ spectroscopic data reported here unambiguously demonstrate the presence of S_3^- at temperatures as low as 100°C. The presence of S_3^- is critical to achieve rapid sulphate reduction, especially at low temperature. We propose that any dissolved constituent which decreases the dielectric constant of water, or which yields favourable S_3^- coordination, will stabilize the trisulphur ion (thus promoting TSR) at T and pH conditions that are less extreme than previously thought. The geometry of S_3^-, similar to ozone, implies to reconsider sulphur isotopic fractionation pathway and may bring new interpretation for the evidence of mass-independent sulphur isotopic compositions recorded in natural and/or experimental TSR-related samples[7,8].

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E-mail address: Laurent.truche@univ-lorraine.fr

What we know and still not know about oceanic salts

Wolfgang Voigt

TU Bergakademie Freiberg, Institute of Inorganic Chemistry, Leipziger Str. 29,
09596 Freiberg, Germany

Abstract

The term “oceanic salts” comprises the salts crystallizing from seawater in course of evaporation, which means salts from combination of the ions Na^+, K^+, Mg^{++}, Ca^{++}, Cl^-, SO_4^{--} with or without water of hydration. Geologists prefer the term “marine evaporites”. Considering precipitation processes from seawater from the very beginning at least the carbonate of calcium and its sensitive relationship to dissolved CO_2 should be included as important constituents. Crystallization and dissolution of these salts from and in complex composed aqueous solutions plays a key role in understanding the genesis of marine evaporitic deposits and to plan technological actions in these environments as for instance in potash mining, in safety management of exhausted potash or rock salt mines, the extraction of potash from brines or in safety assessment of rock salt formations for underground-storage of nuclear and toxic wastes. Thereby, modern technology expects from chemical science a quantitative description of equilibrium and non-equilibrium processes within the complete hexary oceanic system in a broad range of temperatures. For other areas of science technology as for lithium extraction from salt lakes, salt weathering of building materials, development of salt-withstanding building materials, scaling control in natural gas and oil recovery, climate or planetary research need to consider interactions of the oceanic salts with other components (hydroxides, Li^+, Ba^{++}, Sr^{++}) or at extreme temperatures or pressures.

A first complete thermodynamic equilibrium model of the hexary oceanic system based on Pitzer’s ion interaction equations was published in 1980 and 1982 by Eugster, Harvie, Möller and Weare valid for $T = 298$ K. An extended version including CO_3^{2-}, HCO_3^-, CO_2, H^+ and OH^- appeared in 1984 and is widely applied until now and considered as a standard model.

Later for subsystems Pitzer-based models have been developed for enhanced (Greenberg, Möller, Christov) and cryogenic (Spencer, Marion) temperatures. The complete system including H^+ and OH^- is now covered with the THEREDA database valid for temperatures between 273 – 383 K.

Reviewing these solubility models their possibilities and limitations will be discussed. Calculated solubilities and compositions of invariant points will be compared with available experimental data and “model-free” data compilations from D’Ans, Usdowski and Cohen-Adad. At the examples of the $CaSO_4$-containing salt phases as gypsum, anhydrite, goergeyite, polyhalite and glauberite necessary model adaptions due to new data and observations are proposed.

The oceanic salt system belongs to the best investigated inorganic multi-component system. However, near future tasks remain: removal of conflicting data in the extension of crystallization fields of sulphates, establishing of reliable distribution laws for trace elements (bromine, rubidium, lanthanides) between crystals and solution and most challenging the development of means to estimate transition kinetics from metastable to stable equilibria. In addition, it would be worthwhile to pay more attention to pressure effects on crystallization.

E-mail address: Wolfgang.Voigt@chemie.tu-freiberg.de

Supercritical phase equilibria in the system Li_2SO_4 – LiCl – H_2O

Sergey Makaev, Marina Urusova, Vladimir Valyashko

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow

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Abstract

Ternary system Li_2SO_4 – LiCl – H_2O consists of two binary water-salt systems of various types: LiCl – H_2O (1^{st} type) and Li_2SO_4 – H_2O (2^{nd} type). The phase diagram of binary water-salt system of type 1 is characterized by only one field of the three-phase equilibrium (g-l-s_{salt-1}) and a monovariant critical curve (g=l). In the case of binary systems of type 2 there are three-phase equilibria with presence of solid phase ((g-l-s_{salt-2}) and (l_1-l_2-s_{salt-2})), and two monovariant critical curves (g=l) and (l_1=l_2) are completed by critical end-points **p** (g=l-s_{salt-2}) and **Q** (l_1=l_2-s_{salt-2}). Supercritical fluid (SCF) equilibria, where the fluid phase has a homogeneous state at any pressures up to solid saturated solution in two-phase condition (fl-s_{salt-2}), occurs in a temperature range between $T_\mathbf{p}$ and $T_\mathbf{Q}$.

Ternary water-salt systems with salts of two different types (1 and 2) have several regions with the special configuration of phase equilibria. The regions of three-phase equilibria (g-l-s_{salt-1}) and (g-l-s_{salt-2}) is adjacent to binary subsystems of type 1 and type 2 (for latter only at temperatures up to T_p), whereas the region of equilibrium (l_1-l_2-s_{salt-2}) is adjacent to binary subsystem of type 2. Three-phase regions (g-l-s_{salt-2}) and (l_1-l_2-s_{salt-2}) of the ternary system are separated by the two-phase SCF equilibrium (fl-s_{salt-2}). The compositions of solid saturated vapor (gas) and solid saturated liquid solutions (g-l-s_{salt-2}) become closer to each other with increase of temperature and pressure until the critical phenomena (g=l-s_{salt-2}) emerge. The three-phase equilibrium solutions (l_1-l_2-s_{salt-2}) develop with increase of temperature and decrease of pressure up to the compositions of saturated liquid solutions in critical phenomena (l_1=l_2-s_{salt-2}).

The ternary monovariant critical curve (g=l-s_{salt-2}) is originated in the binary invariant critical point **p** (g=l-s_{salt-2}). The second ternary critical curve (l_1=l_2-s_{salt-2}) starts in the binary invariant critical point **Q** (l_1=l_2-s_{salt-2}). It was shown [1] that the interaction of ternary monovariant critical curves (g=l-s_{salt-2}) and (l_1=l_2-s_{salt-2}) can be carried out by two different ways – either by a contact of the monovariant critical curves in double homogeneous critical point (g=l-s_{salt-2}) <=> (l_1=l_2-s_{salt-2}) or by an appearance of four-phase equilibrium (g-l_1-l_2-s_{salt-2}). In the last case a four-phase monovariant equilibrium and a three-phase immiscibility region (g-l_1-l_2) take place in the ternary phase diagram, along with the tricritical point (g=l_1=l_2).

The experimental results for the ternary system Li_2SO_4 – LiCl – H_2O have supported the second version of phase behavior. It was shown that two three-phase regions (g-l-s_{Li2SO4}) and (l_1-l_2-s_{Li2SO4}) exist at 450 and 470°C, however at 470°C these regions are very close to each other, specifically the critical pressures for equilibria (g=l-s_{Li2SO4}) and (l_1=l_2-s_{Li2SO4}) are almost identical. It indicates that the two-phase SCF region (fl-s_{Li2SO4}), which has been separated by three-phase regions (g-l-s_{Li2SO4}) and (l_1-l_2-s_{Li2SO4}), is absent at temperatures above 470°C. Four-phase monovariant equilibrium (g-l_1-l_2-s_{Li2SO4}) forms in the vicinity of this temperature and pressure about 50 MPa. The experimental observations show an appearance three-phase unsaturated immiscibility region (g-l_1-l_2) at temperatures 490 – 520°C that is terminated by the invariant tricritical critical phenomena (g=l_1=l_2).

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E-mail address: valyashko@igic.ras.ru

Solubility Database and the Stable and Metastable Solubility Phenomena on the Complex Salt-water Systems

Tianlong DENG,[1] Shiqiang WANG,[1] Yafei GUO,[1,2] Xiaoping YU[1]

[1]Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering,
Tianjin University of Science and Technology, Tianjin, 300457, P.R. China
[2]ACS Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes,
Chinese Academy of Sciences, Xining, 810008, P. R. China

Abstract

Salt lakes in China are mainly located in the area of the Qinghai-Xizang (Tibet) Plateau, and the Autonomous Regions of Xinjiang and Inner Mongolia. The composition of salt lake brines can be summarized to the complex salt-water multi-component system (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+//Cl-, SO_4^{2-}, $B_4O_7^{2-}$, OH^-, HCO_3^-, CO_3^{2-} - H_2O) [1]. However, the phenomena of super-saturation of brines containing sulphates and borates are often found both in natural salt lakes and solar ponds [2,3]. In order to separate and utilize the mixture salts effectively by salt-field engineering or solar ponds in Qaidam Basin, Qinghai province, our studies on the phase equilibria of salt-water systems are mainly focused on the stable and metastable phase equilibria and phase diagrams using the methods of isothermal dissolution and isothermal evaporation at present years [4-12].

In this paper, the solubility database and the stable & metastable equilibrium phenomena of the multi-component aqueous systems (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}//Cl-, SO_4^{2-}, $B_4O_7^{2-}$ - H_2O) with more than 20,000 aqueous systems from the binary to six-component systems between 1910 to 2013 were introduced.

Moreover, the phase diagram calculation for the system (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}//Cl^-, SO_4^{2-} - H_2O) and its subsystems from 273.15 K to 473.15 K was also introduced on the basis of Pitzer and its extend HMW model.

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E-mail address: tldeng@tust.edu.cn

Phase diagram determination of the key Salt Lake brine system Li^+,Mg^{2+}//Cl-,SO_4^{2-}-H_2O and its industrial application

Dewen Zeng,[1,2] Hongxia Li[2]

[1]College of Chemistry and Chemical Engineering, Central South University, Lu Shan Nan Lu 932#, Chansha 410083, P.R.China
[2]Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xinning Lu 18#, Xining 810008, P.R.China

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Abstract

After solar pond processes, a complicated Li^+, Na^+, K^+, Mg^{2+}//Cl^-,SO_4^{2+}–H_2O type salt lake brines can shrink to be the reciprocal quaternary system Li^+, Mg^{2+}//Cl^-,SO_4^{2+}–H_2O, the solubility phase diagram of which decides the Mg:Li ratio of the brine one can obtain using the solar pond technique without massive loss of Li. Although the key system has been widely investigated for a long time [1-4], no consistent conclusion can be drawn. In this work, we have paid exhaustive effort to measure the solubility diagram of the key system at 298.15 K, and special effort has been paid to determine the $MgSO_4{\cdot}H_2O_{(s)}$ stability field. A Pitzer-Simonson-Clegg model was chosen to represent and predict the solubility phase diagram of the reciprocal quaternary system. It was found that the predicted results agree with our experimental results at 298.15 K. The determined phase diagram of the reciprocal quaternary system can reasonably explain why the Mg:Li mass ratio of a brine can decrease to about 20:1 by a conventional solar pond process, however, 7:1 could be reached when $MgSO_4{\cdot}H_2O_{(s)}$ crystal seed is added to avoid the Li salt loss as $Li_2SO_4{\cdot}H_2O_{(s)}$. The model predicted results show that the increasing temperature favorite the decrease of the Mg:Li mass ratio, and a ratio of 1~2:1 could be reached at optimal temperature.

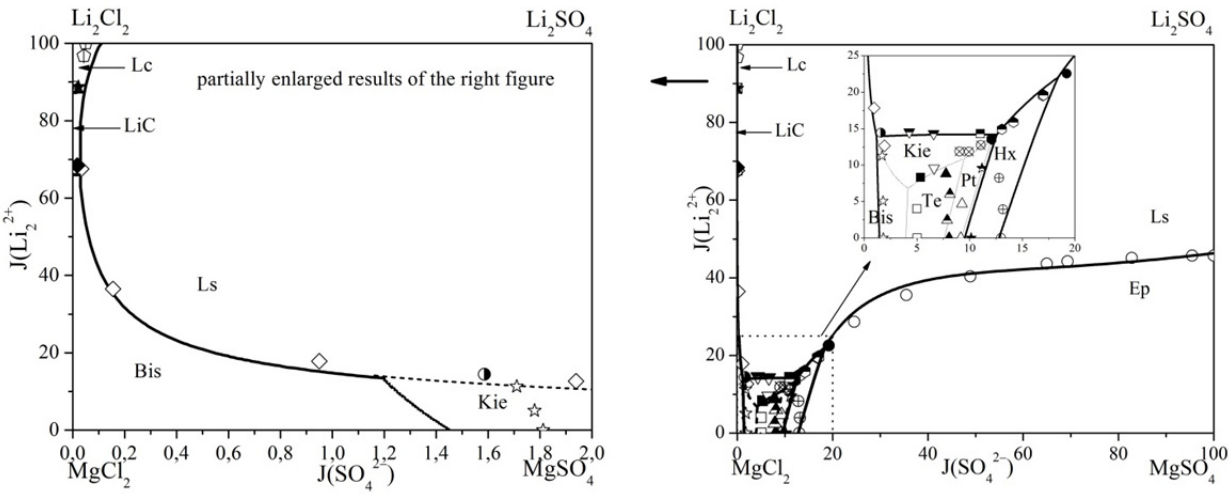

Figure 1 *Dry-salt phase diagram of the quaternary system Li^+,Mg^{2+}//Cl^-,SO_4^{2-}–H_2O at 298.15 K.*

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E-mail address: dewen_zeng@hotmail.com

The united phenomenological model of the electrolyte aqueous solutions structure

M.K. Khripun, O.N. Pestova, L.A. Mund

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

Abstract

According to the ideas of Mendeleev D.I., the solution - is a complex, chemical equilibrium system consisting of the solvent and dissolved substance and products of their interactions. With increase in concentration of salt (dissolved substance), consecutive structural changes of the solution occur. Therefore, it is impossible to describe the whole concentrated area of solution by the one common mathematical model. It is necessary to create a united phenomenological model, which would be applicable in any concentration area of the solution and would precisely interpret experimental results of different physical-chemical methods.

Over the past 35 years, the model concepts about the structure of solutions in all concentration range have been developed using of own results and literature data. At the heart of the model lies a view of solubility polytherm: the phase diagram of dependence solution freezing point from salt concentration. Eutectic composition corresponds to a special point on a polytherm and divides the all concentration range into areas of different dominating structures: water structure (dilute solution) and that of certain crystalline hydrate or the anhydrous salt (concentrated solution). In the last one, water is not a solvent, but it is a part of a new dominant structure. In concentrated solution the inhomogeneity take place, caused by consecutive changes of dominating associates. There is a dynamic balance between them and it is reflected in a course of crystallization branches on solubility polytherm.

The efficiency of the phenomenological model for the salt solutions of different nature has illustrated in a wide concentrations range. The definition of a concentrated solution has given. By means of various physical and chemical methods has shown that the structural unit of a concentrated solution (named sybotactic group SG) is a precursor of the solid phase crystallized from solution by cooling. Composition and structure of the SG in solutions corresponds to that of elementary crystal cell of solid phase, precipitated from solution. The studying of three-component systems has shown that the formation of double salts occurs when there is a structural compatibility of sybotactic groups and common system of bonds take place. The structural incompatibility of SG leads to the microheterogeneity.

E-mail address: Pestova-1980@mail.ru

On the Crystallization Kinetics of Highly Soluble Salts

Chr. Balarew, S. Tepavitcharova, D. Rabadjieva and S. Kamburov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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Abstract

For the spontaneous crystallization of highly soluble salts, a sufficiently high concentration of certain ionic species (complexes) or clusters has to be created in the solution, so that their grouping could yield a suitable crystal nucleus in a reasonably short time. The lowest critical supersaturation needed for nucleation and the highest rate of crystallization is displayed by those salts whose complexes in the solution have analogues in the crystal structure of the crystallizing salt, i.e., when the structure and the composition of the complexes enable their incorporation into the crystal lattice of the crystallizing salt with minimum changes.

4. This concept was confirmed by the studies on the crystallization kinetics of salts in the system $Na^+/Mg^{2+}/SO_4^{2-}/Cl^-$-$H_2O$ [1] and by the parallel Raman spectroscopic studies of the microstructure of these solutions [2]. It was established that upon increasing the concentration of Mg^{2+} ions and respective lowering of the water activity in the solution the variety of the SO_4^{2-} complexes increases. A direct correlation was found between the presence of various SO_4^{2-} associates and the crystallization kinetics of the corresponding salts in this system.

On this basis the phenomena of supersaturation of the solutions, the width of metastable zones, the mechanism of crystallization of metastable phases according to the Ostwald step rule, the differences in the crystallization sequence of salts from marine solutions between the equilibrium solubility diagram and in the case of solar evaporation of marine waters [3], the crystallization of higher hydrates than those stable under the corresponding conditions [4] are interpreted.

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E-mail address: balarew@svr.igic.bas.bg; *Fax:* +359 2 870 50 24

Thermodynamics of lanthanide halide + alkali halide binary mixtures: Experimental and chemometric study

Slobodan Gadžurić,[1] Marcelle Gaune Escard,[2] Leszek Rycerz,[3] Krishna Rajan[4]

[1]Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad,
Trg D. Obradovića 3, Novi Sad, Serbia
[2]Polytech Marseille, IUSTI, CNRS UMR 6595, Mecanique Energetique, Technopole de Château Gombert,
5 Rue Enrico Fermi, 13453 Marseille Cedex 13, France
[3]Chemical Metallurgy Group, Wroclaw University of Technology, 50-370 Wroclaw, Poland
[4]Combinatorial Sciences and Materials Informatics Collaboratory (CoSMIC), NSF International Materials Institute,
Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA

Abstract

The lanthanide halides are attractive components for doses in high-intensity discharge lamps and new highly efficient light sources with energy saving features. Photoluminescence and photo-stimulated luminescence of lanthanide-doped materials induced recently active research targeted to commercial X-ray storage phosphors, while laser activity has been achieved very recently in lanthanide-doped bromide host crystals. The properties of many of the rare earth halides, however, are poorly characterised. The bromides have received even less attention in the scientific literature than the chlorides and iodides. Comprehensive thermochemical parameters for the lanthanide tribromides and dibromides are not available in any of the standard compilations of thermodynamic properties. Accordingly, intensive efforts are being made at an international level both in R&D aspects and also in database development.

The present work is a part of the large program focused on thermodynamic properties, structure and electrical conductivity of lanthanide halides and lanthanide halide – alkali metal halide systems. The thermodynamic properties (temperature and enthalpy of phase transition, heat capacity of solid and liquid phases) and the phase diagrams of selected $LnBr_2$-MBr mixtures were experimentally investigated by Differential Scanning Calorimetry (DSC). The liquid-liquid enthalpy of mixing was measured by high temperature microcalorimetry for all systems. The electrical conductivity of the liquid mixtures was measured down to temperatures below solidification over the whole composition range.

Since the lanthanides are being widely used as simulants of actinides, the chemometric approach was established as a useful predictive tool for those still unexplored systems. Using a principal component analysis (PCA) we have effectively identified the relationships between the molten lanthanides and molten salt properties.

E-mail address: slobodan.gadzuric@dh.uns.ac.rs

The system $Ni(OH)_2$-$NiCl_2$-H_2O at 25°C and 200°C and relations between basic nickel and magnesium chlorides

S. Bette, D. Freyer, W. Voigt

Institut für Anorganische Chemie, TU Bergakademie Freiberg, D-09599 Freiberg, Deutschland

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Abstract

Knowledge about solubility equilibria in the system $Mg(OH)_2$-$MgCl_2$-H_2O are the basis for the application of sorel phases [1] used as barrier construction material in view of nuclear waste disposal in rock salt formations. Beside the phase stabilities in contact with magnesium containing salt solutions also the stability towards heavy metal ions in appropriate salt solutions is of great interest (reactions of waste components with Sorel phases).

In the row of divalent d3 transition metals from Mn to Zn, Ni is the one, being most similar to Mg in terms of chemical properties, ionic radii [2] and coordination in inorganic salts. Furthermore it is the final product in the β^- decay of ^{60}Co [3]. So systemic investigations in the system $Ni(OH)_2$-$NiCl_2$-H_2O, esp. in terms of occurring solid phases, their solubilities and their ability to form solid solutions with basic magnesium chloride hydrates were started.

The present work shows the initial results of our systematic investigations in the system $Ni(OH)_2$-$NiCl_2$-H_2O at 25°C and 200°C, including solubility data and structural characteristics of occurring basic salts. A comparison of solubility data and structural data with those of the related magnesium phases will be drawn. Moreover the formation and structural data of solid solution series among basic nickel and magnesium chlorides will be presented.

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E-mail address: sebastian.bette@chemie.tu-freiberg.de

A combined TRLFS and EXAFS study on the complexation of Cm(III) and Am(III) with chloride at T = 25 – 200°C

Andrej Skerencak-Frech,[1] Daniel R. Fröhlich,[2] Jörg Rothe,[1] Kathy Dardenne,[1]
Petra J. Panak[2]

[1]*Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, 76021 Karlsruhe, Germany*
[2]*Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*

Abstract

A long term safety assessment of a nuclear waste repository in deep geological formations requires a detailed thermodynamic description of the processes relevant for the migration of the actinides. Due to the radioactive decay of the waste, temperatures of up to 200°C may prevail in the near-field of a waste repository. Although a comprehensive thermodynamic database for different actinides is available at 25°C[1], only little data is given at increased temperatures. Chloride is one of the most abundant ligands available in salt rock formations as well as in certain pore waters of clay rocks. Thus, detailed thermodynamic data of $[An(Cl)_n]^{3-n}$ complex at T = 25 to 200°C is of high importance for a comprehensive long term safety assessment. In the present work the complexation of Cm(III) and Am(III) with Cl^- is studied by means of Time Resolved Laser Fluorescence Spectroscopy (TRLFS) and Extended X-Ray Absorption Fine Structure spectroscopy (EXAFS) at T = 25 – 200°C. The experiments are performed in a custom build high temperature cell for spectroscopic measurements up to 200°C. Details on the cell are given elsewhere.[2]

The molar fractions of the different $[Cm(Cl)_n]^{3-n}$ (n = 0,1,2,3) complexes are determined as a function of $[Cl^-]$ and the temperature by peak deconvolution of the TRLFS emission spectra. The results show that up to 100°C almost no $[Cm(Cl]_n]^{3-n}$ complexes are formed. However, at T > 100°C the chemical equilibrium is shifted distinctively towards higher complexes. In particular the fraction of the $[Cm(Cl)_2]^+$ complex increases strongly, while the molar fractions of the $[Cm(Cl)]^{2+}$ and $[Cm(Cl)_3]$ complexes remain below 5%. The conditional $\log \beta'_2(T)$ values are determined and are extrapolated to zero ionic strength with the specific ion interaction theory (SIT). The so determined thermodynamic $\log \beta^0_2(T)$ values increase by two orders of magnitude in the studied temperature range ($\log \beta^0_2(25°C) = -0.81 \pm 0.35$, $\log \beta^0_2(200°C) = 2.83 \pm 0.09$). The temperature dependency of $\log \beta^0_2(T)$ is fitted by the extended van't Hoff equation, taking into account the heat capacity of reaction. Thus, the thermodynamic data for the overall formation of $[Cm(Cl)_2]^+$ is determined ($\Delta_r H^0_{2,m} = 53.4 \pm 5.8$ kJ/mol, $\Delta_r S^0_{2,m} = 164.9 \pm 7.1$ J/mol·K, $\Delta_r C^0_{2,p,m} = 40 \pm 10$ J/mol·K).

The EXAFS results show no presence of $[Am(Cl)_n]^{3-n}$ complexes at T < 100°C. At 200°C approximately two Cl^- ligands are present in the first coordination sphere of the Am(III) ion. This is in very good agreement with the TRLFS data and verifies, that the $[An(Cl)_2]^+$ complex is the dominant species in solution at 200°C. Furthermore, the structural properties of the $[Am(Cl)_2]^+$ complex are determined at high temperatures.

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E-mail address: andrej.skerencak@kit.edu

Quantitative analysis of physical factors that determine the behavior of activity coefficients of electrolytes

N.A. Tikhonov

Physics Department of Moscow Lomonosov State University, Leninskie Gory, 119992, Moscow, Russia

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Abstract

The model that describes the interaction of hydrated ions in uni-univalent electrolytes at various concentrations and temperatures was proposed. We show that, based on fundamental laws of physics, such as the Coulomb law and the Boltzmann distribution, using well-known published data, it is possible to calculate main physical factors that determine the interaction of ions in the solution, for example, the distribution of electric field and the change of hydrated shells of ions when they approach. On this basis, it is possible to explain the nonmonotonic character of curves that describe the activity coefficients and calculate the coefficients in the range of concentration from zero to several mol/l and the range of temperature from zero to several tens degrees, using minimal experimental information. For example, for the calculation of the activity coefficients of an electrolyte in the whole range of concentrations and temperature, it suffices to know the values of the coefficient only for one concentration at three temperature points. The limits of applicability and consistency of the model were analyzed. The conditions under which ions of distinct sign occupy a stable position relative to each other, i.e., the electrolyte is in the quasi-crystalline state were clarified. The approach proposed is verified by comparing simulation results with a considerable amount of published data.

E-mail address: *niktandr@yandex.ru*

Is the Ionic Liquid Ethylammonium Nitrate Like Water?

Glenn Hefter,[1] T. Sonnleitner,[2] D. A. Turton,[3] A. Ortner,[4] S. Waselikowski,[4]
M. Walther,[4] K. Wynne[3] and R. Buchner[2]

[1]*Chemistry Department, Murdoch University, Murdoch WA 6150, Australia*
[2]*Institut Phys. & Theor. Chemie, Universität Regensburg, D-93040, Regensburg, Germany*
[3]*School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK*
[4]*Dept.Molec. & Optical Physics, Albert-Ludwigs-Universität, D-79104, Freiburg, Germany*

Abstract

The protic ionic liquid ethylammonium nitrate $[EtNH_3^+][NO_3^-]$ (EAN) can in some ways be considered as an archetypal IL. Certainly, since its first investigation 100 years ago by Walden, it is one of the best known. The study of the dynamics of EAN, with its relatively simple structure, provides an opportunity to better understand the behaviour of more complex ILs. However, there is another reason why EAN warrants special attention: this is because it has been proposed as an analogue of that truly mysterious but very important substance dihydrogen monoxide (aka water). The basis for this claim is an apparent similarity between various H-bonding modes that are observed in the far-infrared (THz) region of both substances. However, such spectra are difficult to measure and even more difficult to interpret without detailed knowledge of other possible modes that might exist in this spectral region. This talk will describe the dynamics of EAN and some closely-related compounds over the extraordinarily wide frequency range from 200 MHz to 10 THz (~350 cm^{-1}) obtained by using a combination of dielectric relaxation and optical Kerr-effect spectroscopies. Detailed analysis of these spectra shows that the observed intensities are actually a complex combination of overlapping and probably coupled modes, including H-bond vibrations, cation and anion librations and possibly other cooperative effects; the relationships between EAN and water are not clear-cut.

Actinides / lanthanides separation in molten salt media. Application to the liquid fuel reprocessing of molten salt fast reactor (MSFR) system

D. Rodrigues, S. Jaskierowicz, S. Delpech

Institut de Physique Nucléaire d'Orsay, 15 rue Georges Clémenceau, 91400 Orsay, France

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Abstract

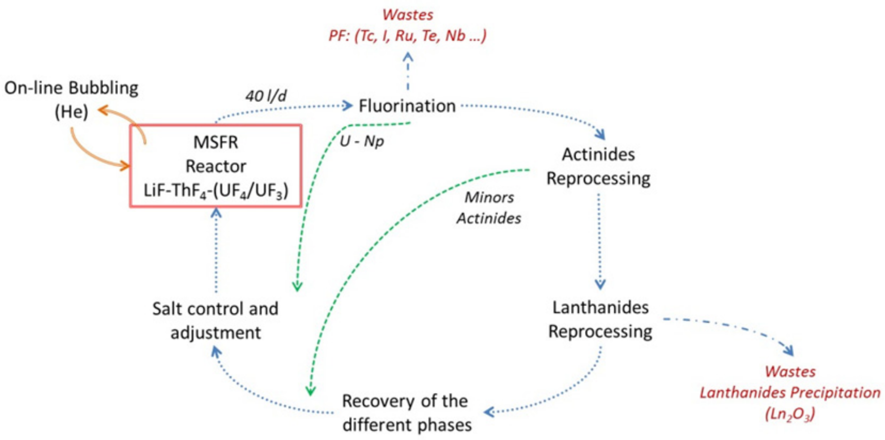
Molten salt fast reactor (MSFR) is an innovative concept of molten salt reactor (MSR) developed by CNRS since 2004 and based on the concept developed in the 1965 by the Oak Ridge National Laboratory (ORNL) of USA. The MSFR concept has the particularity of using a liquid fuel for nuclear energy. This system is based on Th-U nuclear cycle. The fissile material is dissolved in a molten salt mixture, which circulates in the primary circuit and serves both as fuel and coolant. This concept was retained by the Generation IV initiative in 2001, taking advantages of using a liquid fuel which allows more manageable on-line core control and reprocessing fuel cycle flexibility (U or Th) and minimization of radiotoxic nuclear wastes. Then, to develop the fuel reprocessing of the molten salt fast reactor, a world-wide study is in progress in molten chlorides and fluorides salts. One objective is to set-up processes for extraction of fission products (including lanthanides) from the fuel salt and back-introduction of actinides in the fuel salt. In this way, the system is a closed fuel cycle. In this context, electrochemical properties of actinides and lanthanides need to be reassessed.

The main objective of the project is a selective extraction of remaining actinides and lanthanides in spent liquid fuel (Actinides and Lanthanides Reprocessing in the Figure below). Extractions of lanthanides and actinides are performed by a reductive extraction in liquid Bi pool containing metallic lithium as reductive reagent [1].

The efficiency of a reductive extraction depends on the concentration of lithium inside the metallic Bi pool and also on the volume of the metallic phase.

So, it is necessary to determine the best conditions to get the most effective extraction. Thereby, the first study is to find the best way to produce a reductive metallic pool. Secondly is to experiment a reductive extraction of neodymium (0.05 mol%) in LiF-ThF_4 (77.5-22.5 mol%) molten salt by a liquid Bi pool containing metallic lithium.

Thermodynamical and experimental analysis allow to conclude that a fraction of 10 mol% in lithium in the metallic phase has the most effective extraction of lanthanides. The first reductive extraction experiment was realized in static conditions and has shown extraction efficiency of 15% for Nd.



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E-mail address: rodrigues@ipno.in2p3.fr

Retention of radiocarbon by carbon isotope exchange between groundwater and calcite

Janne Lempinen, Jukka Lehto

Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, 00014 University of Helsinki, Finland

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Abstract

Radiocarbon (^{14}C), along with ^{129}I and ^{36}Cl, is one of the key radionuclides when assessing the radiation doses caused to humans and biota by spent nuclear fuel disposal. Its behavior in geosphere, however, is to date not well understood and therefore it is assumed not to be retained in bentonite or bedrock.

The predominant radiocarbon species in groundwater are expected to be dissolved carbon dioxide and methane, but the presence of heavier hydrocarbons cannot be overruled. The solubility of radiocarbon as dissolved carbon dioxide is limited by the solubility of calcite ($CaCO_3$), a common fracture mineral in the bedrock at the Finnish Olkiluoto site. Most of the groundwaters at the site are saturated with calcite [1]. At solubility equilibrium calcite is dissolved and precipitated at equal rates and therefore no net changes in concentrations of calcium or carbonate ions occur. Carbonate radiocarbon entering such system may also be precipitated on fracture surfaces and form a solid solution with the calcite. The reaction equation for the isotope exchange between groundwater and calcite is

$$^{14}CO_3^{2-}\ (aq) + CaCO_3\ (s) \leftrightarrow CO_3^{2-}\ (aq) + Ca^{14}CO_3\ (s).$$

The rate of the retention of carbonate radiocarbon as a function of time was investigated in batch experiments. The experiments were done on calcite in synthetic reference groundwaters [2] and solutions with different Ca^{2+} concentrations. Calcite was first equilibrated with solutions and the solutions were then radiolabelled with a small volume of $^{14}CO_3^{2-}$ tracer solution. The activity concentration of radiocarbon was then observed as a function of time. The pH and Ca^{2+} concentration of the solutions were also determined to verify the solubility equilibrium.

In all the solutions studied an exponential decrease in the activity concentration of radiocarbon was observed. The isotope exchange thus follows first-order kinetics. The rate of the isotope exchange reaction increased with increasing calcium concentration. The half-life of the isotope exchange ranged from a few days in saline groundwater to dozens of days in fresh groundwater and dilute solutions when the ratio of solution to solid calcite was 28 ml/g. The experiments are ongoing to quantitatively describe the relation between the calcium concentration and the rate of retention of carbonate radiocarbon and the results will be presented in the conference poster. Results so far show that the fracture calcite can retain carbonate radiocarbon and delay its transport in bedrock especially in saline groundwater of high Ca^{2+} concentration.

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E-mail address: janne.lempinen@helsinki.fi

Poster contributions

Measurement and modelling caffeine solubility in supercritical CO_2; A theoretical and empirical approach

Pravin Vasantrao Gadkari,[1,2] Manohar Balarman[1,2]

[1]*Department of Food Engineering, CSIR (Council of Scientific and Industrial Research, India)*
- Central Food Technological Research Institute, Mysore-570 020
[2]*Academy of Scientific and Innovative Research, India*

Abstract

The decaffeination of green tea was carried out under supercritical CO_2 with addition of an ethanol entrainer. The experimental solubility of caffeine in supercritical CO_2 varied from 60.96×10^{-6} to 149.55×10^{-6} at pressures (15 to 35 MPa) and temperatures (313 to 333 K). The solubilities of caffeine were predicted using theoretical and semi-empirical models. The theoretical models based on equations of state (EOS) such as Peng Robinson (PR), Soave Redlich Kwong (SRK), and Redlich Kwong (RK) were applied to predict the solubility. Among the three models, RK model had given the best predicted values of solubility with 11.08% of AARD. The maximum solubility of 115.60×10^{-6} was predicted at 25 MPa and 323 K which well agreed with experimental results. It was observed that solubility of caffeine decreased at constant pressure and increasing the temperature of system. Further attempts were made to predict the solubility of caffeine using semi-empirical models such as Chrastil, Yu, Gordillo and coworks, Jouyban and Modified Teja model. It was observed that semi-empirical models gave a good correlation with experimental data. Among all models, Gordillo and coworkers model gave the best fit to experimental data with 1.04 % AARD. It was concluded that solubility of caffeine is not only depending on the temperature but also, it was depending on pressure of the system. Solubility of caffeine in SC-CO_2 was also compared with solubility of pure caffeine in conventional solvents.

E-mail address: manoharb@cftri.res.in

Synthesis, characterization and dissolution thermodynamics of biologically active pyrimidine derivatives in organic solvents at different temperatures

S. Baluja, K.D. Bhesaniya

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

Abstract

Some new biologically active pyrimidine derivatives are synthesized and their structures were confirmed by IR, ^{1}H NMR and mass spectral techniques. The solubility of these compounds has been studied in methanol, N, N dimethylformamide and carbon tetrachloride by gravimetrical method at different temperatures (298.15 to 328.15 K) under atmospheric pressure and the solubility data was correlated with temperature. The solubility is found to increase with temperature and order of solubility is found to be maximum in N, N dimethylformamide and minimum in carbon tetrachloride. The modified Apelblat and Buchowski-Ksiazczak λh equations were used to correlate the experimental solubility data. Further, some thermodynamic parameters such as dissolution enthalpy, Gibb's free energy and entropy of mixing have also been calculated. The positive values of enthalpy and Gibbs energy of solution suggest that the dissolution process to be endothermic and spontaneous.

E-mail address: shipra_baluja@rediffmail.com

Solubility and hydrolysis of Tc(IV) in KCl solutions

A. Baumann, E. Yalcintas, X. Gaona, M. Altmaier, H. Geckeis

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

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Abstract

Technetium-99 is one of the main fission products of ^{235}U and ^{239}Pu in nuclear reactors. Due to its long half-life ($2.1 \cdot 10^5$ a) and redox-sensitive character, ^{99}Tc is a very relevant radionuclide in Performance Assessment exercises (PA) of repositories for radioactive waste. Tc(VII) is the prevailing oxidation state under oxidizing and redox-neutral conditions and exists as soluble and mobile TcO_4^-. On the contrary, Tc(IV) forms sparingly soluble hydrous oxides ($TcO_2 \cdot xH_2O(s)$) under reducing conditions as those expected in deep underground repositories. Potassium is an abundant cation in different types of natural groundwaters. It can also be found in high concentrations (up to 0.6 M) in cementitious environments as considered in concepts for the disposal of low and intermediate level (L/ILW) and high level waste (HLW). In this context, an appropriate understanding and thermodynamic description of Tc(IV) solubility and hydrolysis in dilute to concentrated KCl solutions is required.

In this work, the solubility of Tc(IV) oxyhydroxide phases in dilute to concentrated (0.1 M to 4.0 M) aqueous KCl solutions is investigated within $1.5 \leq pH_c \leq 14.5$. $Na_2S_2O_4$ and Sn(II) were used as reducing agents to ensure that ^{99}Tc is present in oxidation state +IV. [Tc], pH_c and E_h were monitored at regular time intervals up to several months. Solid phase characterization of selected batch experiments were performed by XRD, SEM–EDS and quantitative chemical analysis. Redox speciation of Tc in the aqueous phase was quantified for selected samples using solvent extraction with TPPC.

In all cases and pH regions, the increase of [KCl] significantly impacts the solubility of Tc(IV). Under acidic conditions and low [KCl], the solubility of Tc(IV) defines a slope of –2 indicating the predominance of TcO^{2+} in the aqueous phase in equilibrium with $TcO_2 \cdot 1.6H_2O(s)$. In this region, the increase of ionic strength up to 4.0 M KCl leads to a very significant increase in Tc(IV) concentration which cannot be explained by ion interaction processes but likely indicates the formation of a new species involving complexation with chloride. An unexpected increase in Tc(IV) solubility takes place with increasing [KCl] under near-neutral pH conditions where the formation of the neutral species $TcO(OH)_2(aq)$ is predicted by the NEA–TDB [1]. This new and surprising effect is further evidenced by experiments in KCl–NaCl mixtures of constant ionic strength but increasing KCl/NaCl ratios where a clear dependence on the K^+ concentration is observed. The effect can be properly explained by defining the aqueous species $KTcO(OH)_2^+$ according to the solubility reaction $TcO_2 \cdot 1.6H_2O(s) + K^+ \Leftrightarrow KTcO(OH)_2^+ + 0.6H_2O$. For each investigated KCl concentration, the solubility of Tc(IV) under hyper-alkaline pH conditions follows a well-defined slope of +1, indicating the expected formation of the anionic hydrolysis species $TcO(OH)_3^-$.

The present work provides comprehensive chemical, thermodynamic and activity (SIT) models of Tc(IV) solubility and hydrolysis in acidic to hyper-alkaline KCl media.

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E-mail address: alexander.baumann@student.kit.edu

Crossover Peng-Robinson equation of state for describing the thermodynamic properties of pure fluids near critical point

Hassan Behnejad, Hashem Cheshmpak, Asma Jamali

Department of Physical Chemistry, School of Chemistry, University, College of Science, University of Tehran, Tehran 14155, Iran

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Abstract

In this work, a theoretical method has been introduced for developing the crossover Peng-Robinson (CPR) equation of state (EoS) which incorporates the non-classical scaling laws asymptotically near the critical point into a classical analytic equation further away from the critical point. We have used the cubic Peng-Robinson (PR) EoS as a starting point. The CPR EoS has been adopted to describe thermodynamic properties of some pure fluids (normal alkanes from methane to n-butane and carbon dioxide) such as density, saturated pressure, isochoric heat capacity and speed of sound. Unlike the original application of the crossover transformations made by Chen *et al.* [1], we have introduced the additional term into the Helmholtz free energy to reduce the difference between the classical and non-classical critical properties. It is shown that this new crossover method yields a satisfactory representation of the thermodynamic properties close to the critical point for pure fluids relative to the original PR EoS. As an example, results of the coexistence curves obtained using the crossover and the classical PR EoS together with the original experimental data are presented in Fig. 1.

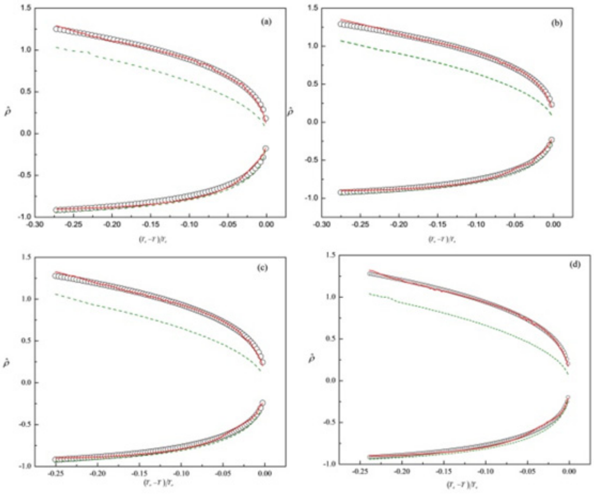

Figure 1 *Coexistence curves for (a) Ethane, (b) Propane, (c) n-Butane and (d) Carbon dioxide. Symbols are experimental data and the results of our CPR EoS (solid lines) and the classical PR EoS (dashed lines).*

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E-mail address: Behnejad@khayam.ut.ac.ir; h.behnejad@ut.ac.ir

Investigation of plasticizing potential of a new biosolvent for cellulose acetate films by DSC & IR-spectroscopy

Adrien Benazzouz,[1] Emeline Dudognon,[2] Natalia T. Correia,[2] Valérie Molinier,[1]
Jean-Marie Aubry,[1] Marc Descamps[2]

[1]Université Lille Nord de France, EA 4478 Chimie Moléculaire et Formulation, Cité scientifique, Bâtiment C6,
59652 Villeneuve d'Ascq, France
[2]Université Lille Nord de France, Unité Matériaux et Transformations UMR CNRS 8207, Cité scientifique, Bâtiment P5,
59650 Villeneuve d'Ascq, France

Abstract

Because of their high glass transition temperature, a lot of polymers require the addition of a plasticizing agent in order to improve their processability. This is the case of cellulose acetate which is a common macromolecule involved in the production of textile fibers, cigarette filters or pharmaceutical tablet coatings [1]. Dimethyl benzene-1,2-dicarboxylate, the methyl ester of phthalic acid (Fig.1 – left), is one of the classical plasticizers of cellulose acetate but it is now questionable in regard to its potential adverse reproductive and developmental effects for humans. Research for green and safe molecular alternatives is therefore relevant. In this study, investigation for a new plasticizer was conducted so as to fill in 3 criteria: compatibility, stability and plasticizing effectiveness.

The compatibility of the small molecule with the polymer was treated with the Hansen approach [2]. This semi-empirical method is a classical way to investigate polymer solubility thanks to the determination of the so-called solubility sphere in the Hansen 3D-space, which encompasses good solvents and excludes the others [3]. A screening of molecules pointed out that dimethyl isosorbide (Fig.1 – right), a sorbitol derivative, could be a promising green and compatible alternative to dimethyl phthalate. The plasticizing effectiveness of dimethyl isosorbide was assessed by monitoring the evolution of the glass transition temperature of cellulose acetate by differential scanning calorimetry (DSC). As the plasticizer efficiency is related to its chemical structure and its ability to weaken intermolecular attractions between the polymer chains, Fourier transform infrared spectroscopy (FTIR) was also used to compare molecular interactions of dimethyl isosorbide and dimethyl phthalate with cellulose acetate. Here, dimethyl isosorbide is shown to display suitable properties to be used as a plasticizer for cellulose acetate instead of dimethyl phthalate.

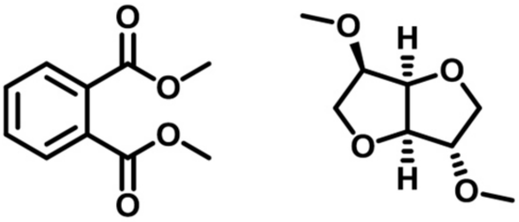

Figure 1 *Chemical structures of dimethyl phthalate (left) and dimethyl isosorbide (right)*

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E-mail address: adrienbenazzouz@aol.com

THEREDA - added value to contaminant speciation in brines

Frank Bok, Anke Richter, Vinzenz Brendler

Helmholz-Zentrum Dresden-Rossendorf e.V., Institute of Resource Ecology, Bautzner Landstr. 400, 01328 Dresden, Germany

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Abstract

The cooperative project THEREDA establishes a consistent and quality assured database for elements, temperature and pressure ranges relevant for (nuclear) waste disposal. Its focus is on repositories in salt host rocks, thus utilizing the Pitzer model for ion-ion-interactions. Data access is possible via http://www.thereda.de including ready-to-use databases for four common geochemical codes (ChemApp, EQ3/6, Geochemist's Workbench, PHREEQC). A first data release was issued in 2011; the newest release covers tetra- and hexavalent uranium data for the system of oceanic salts containing Na, K, Mg, Ca, Cl, S, C, and Si.

The NEA Thermodynamic Database (TDB) [1,2] is the major source for thermodynamic data of the aqueous and solid uranium species. Additionally, recently published papers and partially unpublished works from KIT-INE are considered, also addressing Pitzer parameters [3]. Moreover, the THEREDA data release included thermodynamic data of secondary mineral phases formed in the waste material, which were excluded by [1,2] as a result of very stringent quality demands.

The main focus of the THEREDA database is the provision of data for the correct calculation of the solubility of radiotoxic elements in highly saline solutions. Thus, predictive test calculations for the solubility of uranium minerals for both main redox states of uranium (+IV and +VI) were carried out including other Pitzer databases. Modeling results were compared to experimental solubility data from literature references [4–6] and indicate the high quality of the THEREDA data base itself.

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E-mail address: f.bok@hzdr.de

Solubility of plutonium hydroxides under electrolytic reducing conditions

H.-R. Cho, W. Cha, E. C. Jung, K. Song

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
Daedeok-daero 989-111, Yuseong-gu, Daejeon 305-353, Republic of Korea

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Abstract

The solubility of plutonium hydroxides and the redox behaviors of plutonium in aqueous solutions should be understood to assess the safety of high-level radioactive waste disposals in a deep geological system [1]. Plutonium can easily coexist in solutions as different oxidation species: Pu(III), Pu(IV), Pu(V), and Pu(VI). The redox conditions of plutonium solutions have to be carefully controlled to investigate the chemical behavior of each plutonium oxidation state. Pu(III) is not stable in an aqueous solution and easily oxidized in the atmosphere. In deep geological environments excluding oxygen, however, a reducing condition is predicted and will lead to rather stable Pu(III). The concentration of soluble plutonium species under reducing conditions [2, 3] were higher than the reported concentration of Pu(IV) hydroxide due to the dominant aqueous species of Pu(III), which might hinder the isolation and immobilization of plutonium in the repository.

In the present work, the reduction conditions were controlled through electrolysis. An electrochemical cell with a Teflon vessel and quartz tubes containing electrodes were installed in a glove-box purged with Ar gas to investigate the colloid formation and solubility of plutonium hydroxide at various concentrations of plutonium and hydrogen ions. In the reduction vessel, plutonium was reduced to Pu(III), and the concentration of hydrogen ions was simultaneously decreased by electrolysis without the addition of alkaline solution, which is called a coulometric titration [4]. The oxidation states of plutonium in the solution phase were investigated by measuring the absorption spectra using a spectrophotometer (CARY5, Varian). The freshly generated colloids of plutonium were monitored and the solubility of plutonium hydroxides was determined using LIBD (Laser Induced Breakdown Detection) as previously described [5]. The solubility behaviors of plutonium hydroxides investigated under reducing conditions controlled by electrolysis will be discussed in comparison with those investigated using high-pressure H_2 gas [2, 3] and adding Fe powder [6] to maintain the oxidation states of Pu(III).

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E-mail address: hrcho@kaeri.re.kr

Structural Transformations in $Ca(ClO_4)_2$ Aqueous Solutions at Change Salt Concentration

L.A. Myund, A.G. Davidian, M.K. Khripun

Department of Inorganic Chemistry, Faculty of Chemistry, Saint-Petersburg State University, Russia

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Abstract

A new approach to the study of the structure of electrolytes aqueous solutions was developed. Structural transformations in electrolytes aqueous solutions as the concentration were found.

We use the methods of absorption spectroscopy in the near infrared (NIR) and attenuated total reflection in the mid infrared (ATR). Prospects of applying these methods to the study of water systems in the areas of manifestation of valence ν_{OH} (H_2O) (NIR, ATR) , deformation $\delta(H_2O)$ (ATR) and the natural oscillations of the ion ClO_4^-(ATR) is related to the possibility of obtaining for a series of solutions of different concentrations of quantitative data necessary for the subsequent chemometrics.

The approach to the interpretation of spectral data based on the submissions of the existence of aqua ions, solvent-separated and contact ion pairs in solutions is not promising in the case of broad and unresolved stretching bands of water and anti-symmetric stretching vibrations Cl-O ion ClO_4^-. Methods PCA and MCR-ALS are applied for experimental data processing. The important advantage of that is the possibility of calculations of the spectra forms and distribution of the spectral forms depending on the solution concentration without postulating material balance equations and the law of mass action.

We think that solution is a complex system, consisting of water and salt hydrates in dynamic equilibrium In this approach, the relationship between the spectra and solubility polyterm exists through the transformation of the spectra using chemometrics and phenomenological model of the structure of concentrated aqueous solutions. According to this model, structural microinhomogeneity in calcium perchlorate solutions should be observed because at 25°C in a solution, there are three qualitatively different concentration range, where structure pure water and structures cybotactic groups based on the tetrahydrate and hexahydrate calcium perchlorate dominate.

Thus, NIR and ATR spectra of calcium perchlorate aqueous solutions were studied in a concentration range of 0.22 - 4.3 M (0.22 - 7.46 m) at 25°C. Structure of tetrahydrate calcium perchlorate crystallized from saturated at 25°C aqueous solution was established by X-Ray analysis. New approach to the study of concentrated aqueous electrolyte solutions is proposed. By the methods of Principal Component Analysis (PCA) and Multivariate Curve Resolution - Alternating Least Squares (MCR-ALS) the number, spectra, and concentration profiles of spectral forms of water and ClO_4^- ion were determined in the solutions. Found: concentration ranges of structure reorganization of the solution, the nature of structural inhomogeneity, various states of ClO_4^-ion in the regions of domineering water own structure and cybotactic groups based on calcium perchlorate hexa- and tetrahydrate, the existence of a system of hydrogen bonds of solid tetrahydrate in the saturated solution of calcium perchlorate.

E-mail address: AGDavidian@yandex.ru

Phase equilibria of the ternary system $Li_2SO_4 – Li_2B_4O_7 – H_2O$ at 288.15 K

S.Q. Wang,* B. Fan, Y.F. Guo, T.L. Deng

Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering,
Tianjin University of Science and Technology, Tianjin, 300457, P. R. China

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Abstract

Salt lakes in China are mainly distributed in the regions of the Qinghai-Xizang(Tibet) Plateau, Xinjiang and Inner Mongolia with abundant resources of lithium, magnesium, potassium, boron and so on [1]. It belongs to the complex muti-component aqueous system ($Li-Na-K-Mg-Ca-H-Cl-SO_4-B_4O_7-OH-HCO_3-CO_3-H_2O$). Salt-field engineering and solar ponds have been adopted as the technical process of exploitation and utilization for salt lake brine in order to make full use of various inorganic salt resources [2-3].

The phase equilibria of the ternary system $Li_2SO_4–Li_2B_4O_7–H_2O$ were studied at 288.15 K by the isothermal solution equilibrium method. The solubilities and the physicochemical properties including density and pH value of the equilibrium solution were determined. On the basis of the experimental results, the stable phase diagrams and the diagrams of physicochemical properties versus composition were plotted. The metastable phase diagram of the quinary system shows in Fig. 1. In the phase diagram of the ternary system at 288.15 K, there are one invariant point, two variant curves, and two crystallizing zones corresponding to lithium sulfate monohydrate ($Li_2SO_4·H_2O$), and lithium tetraborate trihydrate ($Li_2B_4O_7·3H_2O$). There were no double salts or solid solutions formed in this system, and it belongs to the simple hydrate type-I. The density and pH value of the equilibrium solution change regularly with the increasing composition of lithium sulfate in the solution.

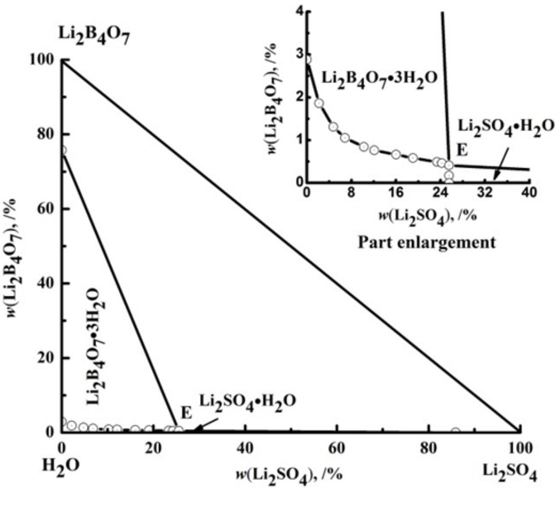

Figure 1 *Phase diagram of the quinary system ($Li^+,Na^+,Mg^{2+}//Cl^-,SO_4^{2-}-H_2O$) at 273.15K; Lc, $LiCl·H_2O$; Lic, $LiCl·MgCl_2·6H_2O$; Bis, $MgCl_2·6H_2O$.*

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*Corresponding author
E-mail address: wangshiqiang@tust.edu.cn

Phase equilibria of the ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at 288.15 K

Y.F. Guo,[1,2] W. Qiao,[1] S.Q. Wang,[1] X.J. Hu,[1] T.L. Deng[1]

[1]*Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering,*
Tianjin University of Science and Technology, Tianjin, 300457, P.R. China
[2]*Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes,*
Chinese Academy of Sciences, Xining, 810008, P.R. China

Abstract

Salt lakes in China are characterized by huge amounts, large areas, rich resources and complete type, and they are the important treasury of inorganic salts [1]. In recent years, the developing of lithium and magnesium resources has achieved greatly progress. Along with the change of the structure of resources, lithium-containing brine has become the main approach to produce lithium salts. It is well known that phase diagram plays important roles in the exploiting of salts lake resources [2-4].

In the paper, the phase equilibria of the ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at 288.15 K were studied with the method of isothermal dissolved equilibria. The solubilities and physicochemical properties including density and pH value in the ternary system were determined experimentally. On the basis of the experimental results, the phase diagrams was plotted and shown in Figure 1. In the ternary system at 288.15 K in Fig.1, there is one invariant point, two variant curves, and two crystallizing zones corresponding to lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$, Ls) and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, Eps). Neither double salts nor solid solutions are found, and it belongs to a simple hydrates type-I. The density and pH value of the equilibrium solution change regularly with the increasing composition of magnesium sulfate in the solution. When compared with the isothermal equilibrium phase diagram at 298.15 K [5], the area of the crystallization region of $MgSO_4 \cdot 7H_2O$ is decreased, and $Li_2SO_4 \cdot H_2O$ crystallization area is increased, respectively.

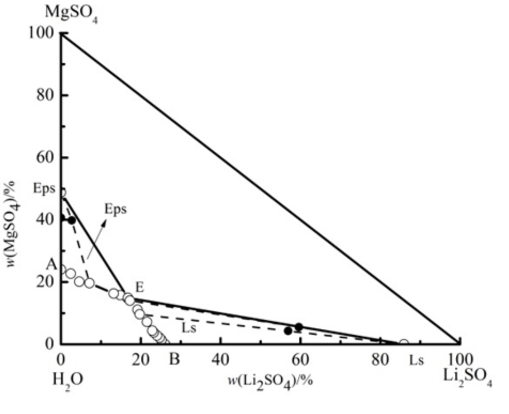

Figure 1 *Phase diagram of the ternary system at 288.15 K. ●, wet residual point;*
○, liquid phase point; Eps, $MgSO_4 \cdot 7H_2O$; Ls, $Li_2SO_4 \cdot H_2O$.

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Acknowledgments

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E-mail address: tldeng@tust.edu.cn

Liquid-liquid Phase Equilibria of Mixed Organic Solvent + Lithium Chloride + Water at $T = 298.15$ K

Daolin Gao, Nan Zhang, Yafei Guo, Xiaoping Yu, Shiqiang Wang, Tianlong Deng

Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering
at Tianjin University of Science and Technology, Tianjin, 300457, P.R. of China

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Abstract

Lithium is the lightest metal and is known as a “energy and strategic metal”. Lithium and its salts have a wide application prospect in various industrial fields, especially in lithium-ion battery and nuclear energy fields [1-2]. Due to the lithium-containing solid ores are drying up gradually and the increasing recoverable cost, developing the lithium-containing brine resources has become an inevitable tendency in the future. On the one hand, separation and extraction of lithium from low Mg/Li ratio brine have successful industrialization through adding lime, sodium carbonate or sodium sulfate to remove magnesium ion, and then lithium carbonate was obtained by adjusting the pH value [3]; on the other hand, recovery of lithium from high Mg/Li brine has been a worldwide problem, seriously restricting its applications.

Solvent extraction as an environmentally friendly, effective and economical method has become a hot technology for recovery of lithium. Liquid-liquid equilibria (LLE) data provided important means to develop, design the equipment and to optimize the extraction process, and it also can be used to obtain thermodynamic models parameters which can be used to simulate the extraction process with the appropriate software [4]. As the chemical composition of lithium ion in the brines was no more than 6.0 g/L. Hence, the LLE data and densities, refractive indexes for the low concentration of lithium chloride phase regions of the ternary system{mixed organic solvent (triisobutyl phosphate, 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, kerosene) (TEK) + lithium chloride + water} and {mixed (triisobutyl phosphate, N-propyl-methyl piperidinium bis[(trifluoromethyl)sulfonyl]imide and kerosene) (TNK) + lithium chloride + water} were determined at $T = 298.15$ K and $P = 0.1$ MPa. A comparison of LLE phase diagrams for the ternary system TEK + LiCl + H_2O and TNK + LiCl + H_2O at 298.15 K and 0.1 MPa was presented in Figure 1.

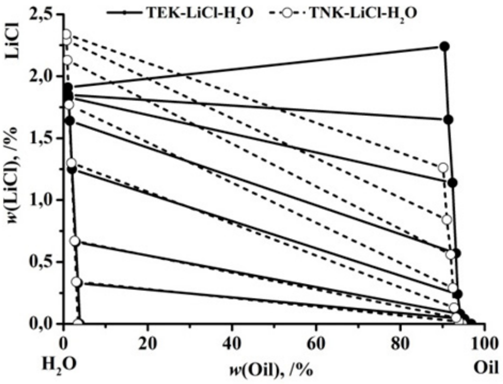

Figure 1 *Comparison of LLE phase diagrams for ternary (TEK + LiCl + H_2O) and (TNK + LiCl + H_2O) system at 298.15 K and 0.1 MPa.*

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*Corresponding author
E-mail address: wangshiqiang@tust.edu.cn

Vibrational spectroscopy analysis of borates in boron-rich brine during dilution and acidification

Xiaoping Yu, Yafei Guo, Tianlong Deng

Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering,
Tianjin University of Science and Technology, Tianjin, 300457, P.R. of China

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Abstract

It is well known that boron exists as polyborate anions in aqueous solution. So, the borate aqueous solutions are more complicated than that of general salts [1]. FT-IR and Raman spectrometry are usually used to study the aqueous solution structure of borates of high boron concentration [2-4]. In this work, boron content and its forms in boro n-rich brine during dilution and acidification in the mother liquor after potassium separating were studied by ICP-OES and Raman spectroscopy.

According to the behavior of borates in brine during dilution, it was found that pH of boron-rich brine is increased with the increasing of dilution ratio, but the amplitude gradually weakened (Fig. 1). Meanwhile, borates in brine gradually transform from high polyborate anions to oligomeric polyborate anions with the increasing of pH according to the change of Raman Spectrograms during dilution. Meanwhile, it was found that pH of boron-rich brine presented obvious decrease at certain range during acidification (Fig. 2). Boron was almost completely precipitated at pH approximately 1.4 according to the relationship between pH and boron content, thus the optimum acidity for boron precipitation is about 1.4. Borates presented slightly change from oligomeric state to high polyborate state based on the change of Raman spectrograms during acidification. However, it is noted that Raman Spectrometry is not sensitivity for low concentration of boron solution.

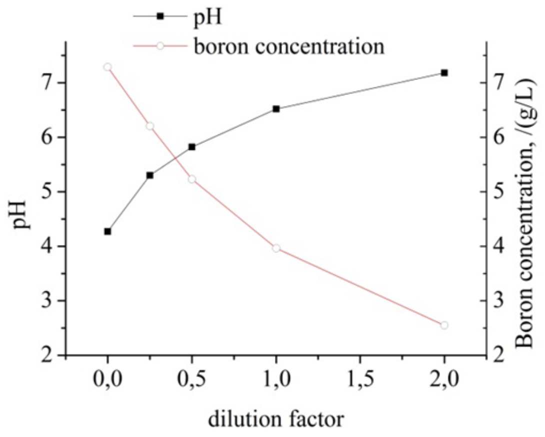

Figure 1 *Relationship between dilution factor of boron –rich brine and pH/boron content.*

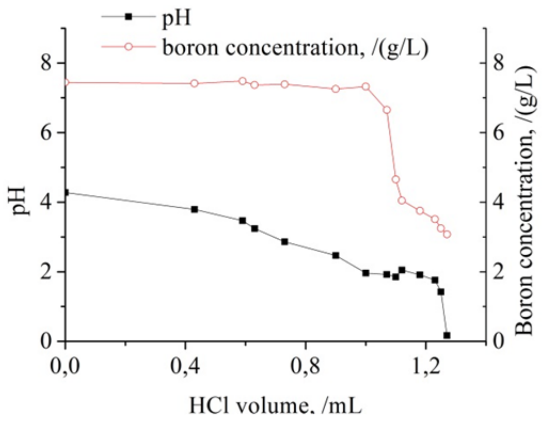

Figure 2 *Relationship between adding HCl in boron–rich brine and pH/boron content.*

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E-mail address: tldeng@tust.edu.cn, Tel/Fax: 86-22-60602963

Thermodynamic description of the system Ca^{2+}–Na^+–H^+–gluconate$^-$–OH^-–Cl^-–H_2O: SIT and Pitzer approaches

Xavier Gaona,[1] Attila Pallagi,[2] Christian Adam,[1] Melanie Böttle,[1] Peter Kaden,[1]
Gábor Peintler,[2] Pál Sipos,[2] Marcus Altmaier[1]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany
[2]Materials and Solution Structure Research Group, University of Szeged, H-6720, Szeged, Dóm tér 7 (Hungary)

Abstract

Gluconic acid (2,3,4,5,6-pentahydroxyhexanoic acid, $C_6H_{12}O_7$ / $HGH_5(aq)$) is a polyhydroxy-carboxylic acid with many applications in the food, pharmaceutical, dye, metal and cement industries, among others. These applications are mostly related with its weak acid character and the strong complexing capacity of its deprotonated form (gluconate, $C_6H_{11}O_7^-$ / GH_5^-) under near-neutral to hyperalkaline pH conditions. The presence of gluconate in cement and concrete, and the planned use of these materials in some of the concepts for nuclear waste disposal (i.e., repositories for low and intermediate level waste, L/ILW) have also brought awareness during the last decade upon the complexation of gluconate with radionuclides and the potential mobilization of these complexes from the repository into the biosphere.

In the present work, a critical evaluation has been made of the thermodynamic properties of gluconic acid aqueous species and solid compounds in the absence and presence of calcium. The evaluation is based on available literature data, and has been complemented for specific systems with newly generated experimental data using potentiometric titrations with ion selective electrodes, ^1H and ^{13}C NMR and solubility studies. Solid phases controlling the solubility of gluconate in Ca-bearing solutions have been characterized with XRD and SEM–EDS techniques. The outcome is a comprehensive thermodynamic selection for gluconate aqueous species (L_δ, $HGH_5(aq)$, GH_5^-, GH_4^{2-}, $CaGH_5^+$, $CaGH_4(aq)$, $Ca_2GH_2(aq)$, $Ca_3(GH_3)_2(aq)$) and solid compounds ($Ca(GH_5)_2(s)$) relevant from very acidic to hyperalkaline pH conditions. The formation of a so far unknown Ca–OH–gluconate solid phase under hyperalkaline conditions has been hinted from solubility experiments, although structural and thermodynamic characterization of this phase are not yet available. Activity models using SIT and Pitzer approaches have been also derived, and permit to extend thermodynamic calculations in gluconate-bearing systems to concentrated NaCl brines.

The thermodynamic description of the binary Ca–gluconate system is to be considered as a building block essential in the development of thermodynamic models of more complex systems, i.e. ternary systems of the type Ca–M–gluconate, where M stands for a tri- or tetravalent metal ion, such as Ln(III)/An(III) and An(IV).

E-mail address: xavier.gaona@kit.edu

Solubility and hydrolysis of U(VI) compounds at 80°C under acidic to hyperalkaline conditions

Xavier Gaona[1] Marie Marques Fernandes,[2] Bart Baeyens,[2] Marcus Altmaier[1]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany
[2]Laboratory for Waste Management, Paul Scherrer Institut, Villigen PSI, Switzerland

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Abstract

Temperature is one of the parameters that will vary during the different phases of operation of a high level radioactive waste (HLW) repository. Elevated temperature conditions (up to 200°C depending on hostrock system and repository concept) will affect actinide chemistry in the near-field of a HLW repository. The hydrolysis of U(VI) has been thoroughly studied at 25°C. The thermodynamic data selection resulting from the NEA–TDB reviews is thus very complete (as $\log K°$, $\Delta_r G°_m$ or $\Delta_f G°_m$) and includes most of the hydrolysis species expected to form from very acidic to hyperalkaline pH conditions. On the contrary, a very limited number of studies is dedicated to assess the effect of temperature on the hydrolysis of U(VI), which results in enthalpy and entropy data selection in the NEA–TDB being restricted to UO_2OH^+. Very recent calorimetric and spectroscopic studies have extended this list to additional cationic and anionic hydrolysis species. Regarding solid phases, enthalpy, entropy and $C°_{p,m}$ data are selected in the NEA–TDB for $UO_3{\cdot}2H_2O$(cr) based on calorimetric studies. No data are selected for ternary Na–U(VI)–OH solids reported to control the solubility of U(VI) in alkaline conditions.

Undersaturation solubility experiments were conducted with $UO_3{\cdot}2H_2O$(cr) and $Na_2U_2O_7{\cdot}H_2O$(cr) solid phases synthesized and characterized in a previous solubility study at 25°C. All samples were prepared in an inert gas (N_2) glovebox under exclusion of O_2 and CO_2. U(VI) solid phases were distributed in several independent batch experiments (4–5 mg solid per sample), arranged in two series of 0.5 M NaCl–NaOH solutions with $4 \le pH_m \le 7$ ($UO_3{\cdot}2H_2O$(cr)) and $8 \le pH_m \le 12$ ($Na_2U_2O_7{\cdot}H_2O$(cr)) and stored in an oven at 80°C (in a N_2 glovebox). Samples were equilibrated for ~1 year and monitored at regular time intervals for dissolved uranyl, [U], and pH_m. Triplicate aliquots (supernatant, 0.1 μm filtration and 10 kD ultrafiltration) were taken for the quantification of [U] by ICP–MS. After reaching equilibrium conditions, solid phases of selected samples were characterized by XRD, SEM–EDS and chemical analysis.

The results indicate that the total concentration of U(VI) in the saturated aqueous solution under weakly acidic conditions slightly decreases (~0.5 log–units) at 80°C compared to similar solubility experiments at 25°C. XRD, SEM–EDS and chemical analysis confirm the transformation of $UO_3{\cdot}2H_2O$(cr) into a Na-bearing solid phase with Na:U ~0.5. No solid phase transformation takes place for $Na_2U_2O_7{\cdot}H_2O$(cr) under alkaline to hyperalkaline conditions. For this solid phase, a significant increase in solubility (1–2 log units) is observed at 80°C above $pH_c = 9.5$. Similar to 25°C, the total concentration of U(VI) as a function of pH shows a well-defined slope of +1 in the pH_m region 9–12, corresponding to the equilibrium $0.5\ Na_2U_2O_7{\cdot}H_2O(cr) + 2\ H_2O \Leftrightarrow Na^+ + UO_2(OH)_4^{2-} + H^+$. This observation is consistent with the expected increase of hydrolysis of metal ions with increasing temperature as a result of the increase of K_w of H_2O. The combination of slope analysis with accurate solid phase characterization (XRD, SEM–EDS, chemical analysis) allows the development of a thermodynamic model for the system $UO_2^{2+}–H^+–Na^+–OH^-–Cl^-$ at 80°C valid within $4 \le pH_m \le 12$.

E-mail address: xavier.gaona@kit.edu

Liquid-liquid extraction of lactic acid from an aqueous solutions with benzyl alcohol

H. Ghanadzadeh Gilani, F. Borji peydeh

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

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Abstract

Lactic acid is widely used in food, pharmaceutical and chemical industries. It also has been used as a monomer for the production of polylactic acid, a biodegradable polymeric material. Therefore, lactic acid with high purity is required. This organic acid can be produced by the fermentation, but the produced lactic acid in high concentrations has adverse effect on microorganisms. So the lactic acid should be separated from aqueous solution[1]. Solvent extraction due to high distribution coefficient, low energy demand, simplicity is a convenient method for the separation of lactic acid from aqueous solution and has been investigated by several researchers [2,3].

In this paper, liquid-liquid equilibria of the ternary system of (water+lactic acid+benzyl alcohol) were investigated at T=298.15K, and atmospheric pressure. The solubility and tie-line data were measured and the ternary diagrams as a function of temperature are plotted in fig1. The ternary systems investigated display type-1 behaviour of LLE. 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[4]. separation factors were calculated to evaluate the extracting capability of the solvents and given in fig2. The experimental tie-line data were correlated using the NRTL model, and binary interaction parameters were obtained and shown in table1.The average root mean square deviation values between the experimental and calculated data show the capability of these model in simulation of the phase behavior of related ternary systems. The experimental results indicated that the Benzyl alcohol, has relatively low separation factors. However, this quantity is greater than one for the system reported in this work, which means that extraction of lactic acid by benzyl alcohol is possible.

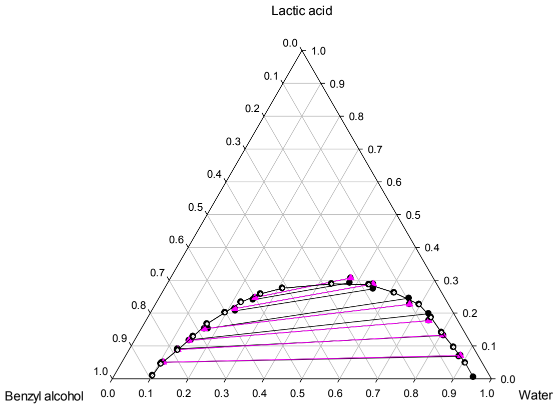

Figure 1 *Phase diagram for [water (1) + lactic acid (2) + benzyl alcohol (3)] at T = 298.15 K; (-○-) experimental solubility curve, (-●-) experimental tie-line data, (–▲–) calculated NRTL data*

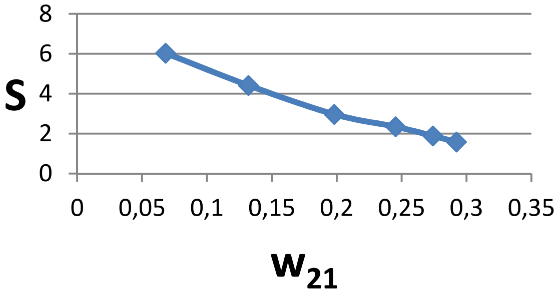

Figure 2 *Separation factor, S, plotted against the mass fraction of lactic acid in the aqueous phase, w21*

Table 1 *NRTL (α= 0.1) binary interaction parameters (bij and bji) and rmsd values for the ternary systems.*

i-j	b_{ij}/K	b_{ji}/K	RMSD (%)
1-2	-4122.95	-425.068	0.812
1-3	2535.92	-827.574	
2-3	-742.31	-3607.73	

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E-mail address: hggilani@guilan.ac.ir

Solubility and hydrolysis of Fe oxides in reducing alkaline to hyperalkaline conditions: Fe(0)–magnetite–Fe(II)$_{aq}$ systems

M. R. González-Siso,[1] X. Gaona,[2] L. Duro,[1] D. Schild,[2] M. Lagos,[2]
G. Darbha,[2] N. Finck,[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, P.O. Box 3640, 76021 Karlsruhe, Germany*

Abstract

Iron will be present in several of the currently considered repository concepts for disposal of radioactive waste as a structural component in reinforced concrete structures, as main component of the steel canisters and as part of the wastes. Anoxic corrosion of Fe is expected to generate very reducing conditions, which will impact the chemical behaviour of the redox sensitive radionuclides present in the waste. In repositories for low- and intermediate level radioactive waste such as SFR in Sweden, the presence of cementitious materials will impose highly alkaline pH conditions to the contacting water. Although an appropriate knowledge of the evolution of the chemical boundary conditions is essential to establish reliable performance assessment models, key uncertainties remain on the redox conditions developed in the presence of iron-bearing materials under hyperalkaline conditions, as well as on the role of corrosion products of Fe in redox buffering. Magnetite (Fe_3O_4) has been identified as one of the main products resulting from the anoxic corrosion of metallic iron and steel. Thermodynamic data selected in the NEA–TDB for this solid phase are based on calorimetric studies. Kinetics have been reported to hinder the solubility equilibrium of magnetite at room temperature under acidic to near-neutral pH-conditions, due to the reversible transformation equilibrium between α-Fe_3O_4(cr) and α-Fe_2O_3(cr). Furthermore, the NEA–TDB does not select any neutral or anionic hydrolysis species of Fe(II) and Fe(III), which are expected to dominate the aqueous chemistry of Fe under hyperalkaline conditions.

In the present study, the solubility of magnetite was investigated at 22 ± 2°C under inert gas (Ar) atmosphere ($O_2 < 5$ ppm). Batch solubility experiments were performed from undersaturation with hydrothermally prepared α-Fe_3O_4(cr). Independent samples were prepared within $8 \le pH_c \le 13$ in 0.1 M NaCl–NaOH solutions. Four different redox systems were defined: S1. α -Fe_3O_4(cr); S2. α-Fe_3O_4(cr) + Fe(cr); S3. α-Fe_3O_4(cr) + 0.01 M $SnCl_2$ and S4. α-Fe_3O_4(cr) + 0.01 M $Na_2S_2O_4$. pH, pe (as pe = 16.9 E_h), $[Fe]_{tot}$ and $[Fe(II)]_{aq}$ were monitored at regular time intervals. Dissolved $[Fe]_{tot}$ and $[Fe(II)]_{aq}$ were measured after 10 kD ultrafiltration using a high-resolution ICP–MS and the ferrozine method, respectively. Solid phases of selected solubility samples were characterized by XPS, XRD, SEM–EDS and AFM.

Very low and reproducible E_h values ($-1 \le$ (pe+pH) $\le +2$) are measured for the magnetite systems in the presence of $SnCl_2$ and $Na_2S_2O_4$. The redox conditions in the system Fe(cr)–α-Fe_3O_4(cr) evolve from (pe+pH) ~ –1 (at $8 \le pH_c \le 9$) to (pe+pH) ~ +3 (at $12 \le pH_c \le 13$). Together with SEM–EDS observations, these results hint towards the possible passivation of the Fe(cr) surface under hyperalkaline pH conditions. Pure magnetite systems retain higher E_h values throughout the complete pH-range evaluated, (pe+pH) ~ +4. XRD confirms the presence of magnetite in all samples. XPS measurements indicate that both the initial material and (most of) the samples after initiated the solubility experiment have a content of 28 ± 3 % Fe(II) in relation to Fe_{tot} on the solid surface, thus approaching the value ideally expected for pure magnetite 33.3 %. The Fe(II) content increases in some samples up to 34 ± 3 %, in combination with the observation of Fe(0) traces by XPS. A particle size of 60–120 nm is quantified by SEM–EDS, AFM and XRD, without significant changes appearing with respect to the initial material. A very significant decrease in the solubility with a log $[Fe]_{aq}$ *vs.* pH_c slope of –2 / –3 takes place within $8 \le pH_c \le 9.5$. For the same pH-region, the solubility significantly increases with decreasing E_h, according with the sequence S2 > S4 > S3 >> S1. A solubility control exerted by the reaction α-$Fe_3O_4(cr) + 8H^+ + 2e^- \Leftrightarrow 3Fe^{2+} + 4H_2O$ is proposed for this pH region. Aqueous iron concentration above pH_c ~10 remains below 10^{-8} M, in spite of the expected formation of negatively-charged Fe(II) hydrolysis species above pH ~11.5.

E-mail address: maria.rosa.siso@amphos21.com

Evolution of chemical species in copper (II) halides – water – organic solvent systems from diluted to saturated solutions and its role in solid phase formation

Artem Gorbunov, Mikhail Skripkin

Institute of Chemistry, Saint-Petersburg State University, Universitetsky prospect, 26, 198504, Saint-Petersburg, Russia

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Abstract

Study of solvation and complexation processes in aqua-organic mixtures is one of actual fields of solution chemistry nowadays. However the regularities of effect of components properties on processes in ternary aqua-organic systems containing d-elements salts and especially on the solution-solid phase equilibria in these systems are not revealed so far. Large experimental data were accumulated in laboratory of Solution chemistry in our research group during last years. In the present communication some regularities between solubility and component properties will be presented.

Processes in liquid phase obviously determines formation of solid phase, its composition and structure. That's why combination of phase and solvation diagrams study is a powerful tool to explain the solubility using not only classical physic-chemical properties of solvents (dielectric permittivity, donor and acceptor ability) but from the point of interactions in liquid phase as well as.

Usually attention of scientists studying aqua-organic saline systems is focused on systems without acidocomplexation (perchlorates, triflates). But this work is devoted to investigation of halide systems where acidopcomplexation plays a significant role and acidocomplexes have different stability (chloride, bromide). It makes possible to reveal the anion nature effect on solvation processes and solubility daigrams in the systems under study. As organic component a set of oxygen-donating solvents with varying main properties and characteristics (donor and acceptor ability, dielectric permittivity, structuring extent, solid angle, etc) was used (dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, tetrahydrofurane). Acetonitrile was chosen for the comparison with already studied systems to confirm technique [1].

An original technique of IR spectra treatment was developed to obtain first solvation sphere composition. It is based on subtraction the ternary solution spectrum from spectrum of mixed solvent with the same composition with some difference factor. This factor shows increase of each solvent content in the bulk during solvation of copper ions. For each solvent specific bands in IR spectrum were chosen for quantitative analysis. Polyhedral types of copper ions were determined by UV-vis spectroscopy.

Composition and structure of equilibrium solids was proved to be dependent from liquid phase processes quantitatively.

Overlap of singular points on solvation diagrams and euthonics on solubility diagrams was observed for several systems.

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E-mail address: artyom-laptop@yandex.ru

Complexation of nickel ions by boric acid and (poly)borates

Anaïs Graff, Martin Bachet

EDF R&D, France

Abstract

Nickel is a corrosion product of major importance in the pressurized water reactor primary circuit because of its activation into ^{58}Co. Precise knowledge of the solubility of corrosion products containing nickel and how it changes with temperature and chemistry would be valuable to understand the transport of nickel from steam generator tubes to the core. Previous experimental studies have focused on the solubility of nickel oxide and nickel metal at high temperatures and pressures in different media including PWR operating conditions [1,2,3], but results are controversial. This study focuses on the complexation of nickel ions by boric acid or (poly)borate ions.

An experiment based on electrochemical reactions and pH monitoring was performed in which nickel ions were gradually formed by oxidation of a nickel metal electrode in a solution of 0,5 mol.kg^{-1} of boric acid. The evolution of pH showed the existence of significant nickel/boron complexation. A tri-borate nickel complex was postulated at high boric acid concentrations when polyborates are present, and complexation constants at different temperatures between 25 and 70°C were determined. However, this tri-borate complex cannot explain the increased solubility seen for NiO/Ni(OH)$_2$ by other researchers at low boric acid concentrations. This suggests that a bidendate nickel boron complex could be formed under those conditions.

The results of this study, when extrapolated to primary circuit temperatures, suggest that complexation of nickel ions by borates can significantly enhance the solubility of nickel metal and nickel oxide. In other words, nickel concentrations at equilibrium with nickel oxides and hydroxides are expected to depend not only on pH, but also on the boric acid concentration. These findings still need to be experimentally confirmed at high temperature.

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E-mail address: anais.graff@edf.fr

Thermodynamic properties for the $MgCl_2{-}MCl{-}H_2O$ (M=Rb, Cs) systems at 298.15 K

L. J. Guo,[1] D. W. Zeng,[1,2] Y. Yao,[1] H. J. Han[1]

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

Abstract

The thermodynamic properties, including the solubility isotherms, for the $MgCl_2{-}MCl{-}H_2O$ (M=Rb, Cs) systems are of great importance for extracting rubidium and cesium resources from Chaerhan salt lake in China. However, the reported solubility data at 298.15 K by different authors [1-5] for each system can not agree with each other, as shown in Figure 1. Meanwhile, the lacking of water activity data for these two systems (for the $MgCl_2{-}CsCl{-}H_2O$ system, the water activities are only in graphical form [5], which are difficult to be evaluated), makes it difficult to judge the solubility data by thermodynamic model. Therefore, we determined the water activities for the $MgCl_2{-}MCl{-}H_2O$ (M=Rb, Cs) systems at 298.15 K by the isopiestic method, and selected the Pitzer model to judge the reliability of the reported solubility data by correlating the measured water activity data.

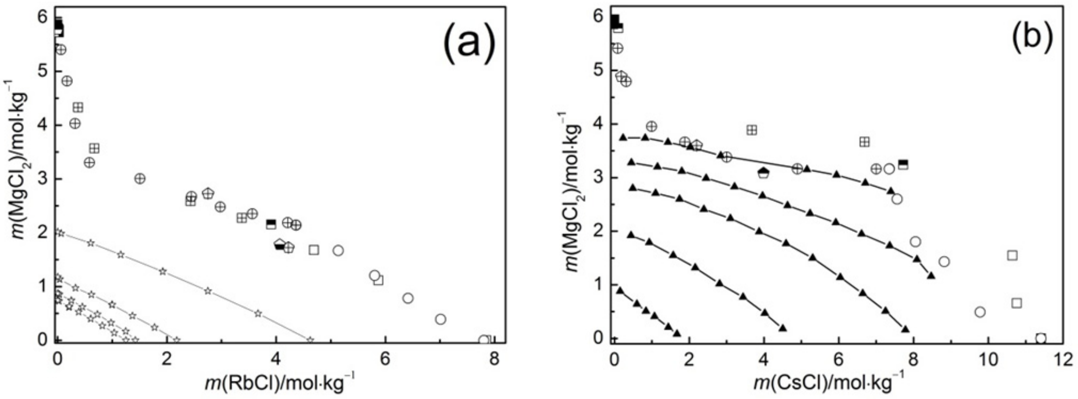

Figure 1 *The solubility isotherms and equal water activity lines for the* $MgCl_2{-}MCl{-}H_2O$ *(M=Rb, Cs) systems at 298.15 K.*
(a) $MgCl_2{-}RbCl{-}H_2O$ *system. ref [1]: ○, RbCl; ⊕,* $RbCl\cdot MgCl_2\cdot 6H_2O$*; ●,* $MgCl_2\cdot 6H_2O$*; ref [2]: ⬟, Eutonic; ⊕,* $RbCl\cdot MgCl_2\cdot 6H_2O$*;*
ref [3]: □, RbCl; ⊞, $RbCl\cdot MgCl_2\cdot 6H_2O$*; ⬒,* $RbCl_2\cdot 6H_2O+RbCl\cdot MgCl_2\cdot 6H_2O$*; ■,* $MgCl_2\cdot 6H_2O$*; −☆−, isopiestic points of this work;*
(b) the $MgCl_2{-}CsCl{-}H_2O$ *system. ref [1]: ○, CsCl; ⊕,* $CsCl\cdot MgCl_2\cdot 6H_2O$*; ●,* $MgCl_2\cdot 6H_2O$*; ref [2]: ⊕,* $CsCl\cdot MgCl_2\cdot 6H_2O$*; ⬟, Eutonic;*
ref [4]: □, CsCl; ⊞, $CsCl\cdot MgCl_2\cdot 6H_2O$*; ⬒, Eutonic; ■,* $MgCl_2\cdot 6H_2O$*; −▲−, equal water activity points and lines[5].*

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E-mail address: l.j.guo@hotmail.com

Solution-solid equilibrium in the systems $MgBr_2 – NR_4Br – H_2O$ (R = Me, Et, nBu)

Ilya Gusev, Mikhail Skripkin, Galina Starova

Institute of Chemistry, Saint-Petersburg State University, Universitetsky prospect, 26, 198504, Saint-Petersburg, Russia

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Abstract

Ternary systems magnesium halide – alkaline halide - water have been the traditional subject of study in Solution Chemistry for a long time. The unique stability of first hydration shell of magnesium cation enables the systematic analysis of the effect of second electrolyte on the properties of ternary systems with domination of hydration processes to be performed. Tetraalkylammonium cations can be regarded to some extent as the continuation of the set of alkaline cations but they exhibit some specific properties that should reflect on the solubility in ternary systems $MgBr_2$ – NR_4Br – H_2O and on the composition and structure of crystallizing double salts.

First of all quite different effects of addition of magnesium bromide on NR_4Br solubility should be mentioned. Increase in anion concentration resulting in increase of cation-anion association of NMe_4Br determines the weak salting-out effect of $MgBr_2$ on the solubility of this salt. This effect is even more pronounced for NEt_4Br where structure-breaking effect of bromine anion and formation of stable aquacation $Mg(H_2O)_6^{2+}$ lead to the breaking of local icebergs around hydrophobic cations that results in strong salting-out effect especially at high concentrations of organic salt. As to the solubility of NBu_4Br that does not change upon the addition of $MgBr_2$, it can be proposed that strongly hydrated Mg^{2+}-cation and Br^--anion have opposite effect on the cation-cation association and as the result their influences compensate one another.

As to the solubility of $MgBr_2$, the length of crystallization fields of $MgBr_2·6H_2O$ decrease in the sequence NMe_4Br > NEt_4Br > NBu_4Br that might be due to the decrease of crystal lattice energy of double salt which determines increase in their solubility.

Formation of double salts was mentioned for all MgX_2 – MX – H_2O systems except MgX_2 – NaX – H_2O. To explain the formation and stability of carnallite-like double salts $MX·MgX_2·6H_2O$ Waizumi [1] has introduced crystallographic tolerance factor *t* that should vary from 0.8 to 1.0 for the stable structure. For $NMe_4Br·MgBr_2·6H_2O$ this value is equal to 0.83 that satisfy the condition mentioned above; the existence of this double salts was proved experimentally. For other systems the double salt formation also was established experimentally but their compositions and structures were quite different.

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E-mail address: gusev-i@yandex.ru

Capturing of carbon dioxide using the aqueous solution of N-Methyldiethanolamine (MDEA) blended with 1-butyl-3-methylimidazolium acetate ionic liquid at high pressures

Ali Haghtalab, Abolfazl Shojaeian

Department of Chemical Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran

Abstract

The solubility and absorption rate of carbon dioxide (CO_2) in aqueous solutions of N-methyldiethanolamine (MDEA) with1-butyl-3-methylimidazolium acetate, [bmim][acetate], ionic liquid have been obtained using the static method. For reduction of the regeneration energy requisition, the [bmim][acetate] is used instead of water in the mixtures of the alkanolamine and ionic liquids. At fixed 30 wt% of MDEA, the loading of CO_2 in the [bmim][acetate] + MDEA + water systems was investigated over a wide range of IL concentrations (0–70%), temperatures (303.15 , 343.15 K) and partial pressure of CO_2 (100–4000 kPa). Also, the absorption rate of CO_2 in these mixtures is measured at initial pressure of 500 kPa.

The results revealed that increase in weight fraction of the [bmim][acetate] in aqueous alkanolamine solutions presents an influential impact on the CO_2 loading so that at low pressures, the results show that the CO_2 loading reduces with increasing of the [bmim][acetate] concentration with keeping fixed concentration of the MDEA. It is due to this fact that in low pressures the chemical absorption is dominated mechanism of the CO_2 absorption so that the presence of more water intensifies the chemical absorption of CO_2. However at high pressures, the physical absorption is dominated so that replacement of the [bmim][acetate] instead of water at fixed concentration of MDEA leads to improve the CO_2 loading due to this fact that the physical absorption of CO_2 by the [bmim][acetate] is higher than water. Also, the results show that the absorption rate of CO_2 decreases with increasing in [bmim][acetate] concentration in [bmim][acetate] + MDEA + water systems at 303.15 and 343.15 K.

E-mail address: haghtala@modares.ac.ir

Solubility and spectroscopic study of An^{III}/Ln^{III} in dilute to concentrated Na–Mg–Ca–Cl–NO_3 solutions

M. Herm,[1] X. Gaona,[1] Th. Rabung,[1] D. Fellhauer,[1] C. Crepin,[2] K. Dardenne,[1] M. Altmaier,[1] H. Geckeis[1]

[1]*Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany*
[2]*Ecole National Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale, 34296 Montpellier CEDEX 5, France*

Abstract

In long-term 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 geotechnical barriers may prevent formation water from contacting the waste, intrusion of aqueous solutions into a repository has to be taken into account. Porewater in certain sedimentary bedrocks as well as water potentially intruding salt rock repositories will be characterized by high ionic strength and high Na^+, Mg^{2+} and Cl^- concentrations. An(III) and An(IV) are the most relevant actinide redox states under the reducing conditions which develop after the closure of deep underground repositories for nuclear waste. In repositories containing waste from nuclear fuel reprocessing, high concentrations of nitrate (≥ 1.0 M) and slow nitrate reduction kinetics may affect the aqueous speciation of radionuclides and thus impact their mobilization into the biosphere. In this study, the solubility and speciation of trivalent actinides and lanthanides in dilute to concentrated $NaCl–NaNO_3$, $MgCl_2–Mg(NO_3)_2$ and $CaCl_2–Ca(NO_3)_2$ mixed solutions are investigated at repository relevant pH conditions and 22 ± 2°C.

All samples were prepared and stored in Ar glove boxes. Batch solubility experiments were performed from undersaturation with $Nd(OH)_3(am)$. Solid phases were characterized using XRD and SEM-EDX. Nd–L_{III} EXAFS spectra were recorded at the INE beamline at ANKA. Cm(III)–TRLFS measurements were performed with $\sim 10^{-7}$ M Cm(III) per sample.

No significant enhancement in $Nd(OH)_3(am)$ solubility occurs in $NaCl–NaNO_3$ and $CaCl_2–Ca(NO_3)_2$ mixtures compared to nitrate-free systems [1]. A clear increase in solubility occurs for $MgCl_2–Mg(NO_3)_2$ mixtures with $m_{Mg}2+ \geq 2.83$ m, $m_{NO3}- \geq 1.13$ m and pH_m 8–9. Provided the solubility control exerted by $Nd(OH)_3(am)$ (confirmed by XRD and SEM-EDX in all systems with $m_{Cl}- \leq 5.82$ m), the slope analysis of the experimental data in $MgCl_2–Mg(NO_3)_2$ mixtures indicates the formation of aqueous species Mg–Nd–OH–NO_3 with stoichiometries Nd:OH 1:1 ($pH_m \leq 8.3$) and Nd:OH 1:2 ($pH_m > 8.3$). Cm(III)–TRLFS data reveals the formation of aquatic "Cm(III)–OH–NO_3" species with $pH_m \geq 4.94$ only in $MgCl_2–Mg(NO_3)_2$ systems, thus hinting towards the participation of Mg in the complex formation. Moreover confirmed by EXAFS, where the peak at ~4 Å is properly fitted with Mg as backscatterer. Slope analysis, solid phase characterization, Cm(III)–TRLFS and Nd–L_{III} EXAFS observations confirms the relevance of the equilibrium reactions $An^{III}/Ln^{III}(OH)_3(am) + H^+ + NO_3^- + Mg^{2+} \Leftrightarrow Mg[An^{III}/Ln^{III}(OH)_2NO_3]^{2+} + H_2O$ and $An^{III}/Ln^{III}(OH)_3(am) + 2H^+ + NO_3^- + Mg^{2+} \Leftrightarrow Mg[An^{III}/Ln^{III}OHNO_3]^{3+} + 2H_2O$ in concentrated nitrate-bearing Mg–systems and permits to further extend the chemical, thermodynamic and activity models described in [1] for Ln(III) and An(III) to $Ln^{3+}/An^{3+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–NO_3^-$ systems.

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E-mail address: michel.herm@kit.edu

Interaction of An(III/IV/V/VI) with borate in dilute to concentrated alkaline NaCl, $CaCl_2$ and $MgCl_2$ solutions

K. Hinz,[1] M. Altmaier,[1] X. Gaona,[1] Th. Rabung,[1] E. Alekseev,[2] D. Schild,[1] H. Geckeis[1]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany
[2]Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich, 52428 Jülich, Germany

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Abstract

The assessment of the long term safety of a nuclear waste repository requires reliable information about the chemistry and migration behavior of actinides. Boron may be present in repositories for radioactive waste as a component of the emplaced waste. In repositories in rock-salt formations, boron can further be a component of the intruding brine solutions.

In the present work, the interaction of An(III/IV/V/VI) with borate in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions was investigated by a comprehensive series of solubility experiments combined with solid phase characterization and aqueous speciation techniques.

Experiments were performed under inert gas (Ar) atmosphere at 22 ± 2°C. Samples were prepared in 0.1–5.0 M NaCl and 0.25–3.5 M $CaCl_2$ / $MgCl_2$ with $0.004\ M \leq [B]_{tot} \leq 0.4\ M$ and $7 \leq pH_c \leq 13$. Nd(III), ^{232}Th(IV), ^{237}Np(V) and ^{238}U(VI) solubility was investigated in independent batch experiments from undersaturation using $Nd(OH)_3$(am), $Th(OH)_4$(am), NpO_2OH(am,fresh), $UO_3\cdot 2H_2O$(cr) and $Na_2U_2O_7\cdot 1.6H_2O$(cr) as solubility-controlling phases. A synthetic, hydrothermally prepared and well-characterized $Nd[B_4O_{13}(OH)_4]$(cr) solid phase was also investigated from undersaturation and used to define a reference solubility concentration. Samples were equilibrated for up to 142 days; pH_c and metal concentration were monitored at regular time intervals with ICP–MS (Nd, Th, U) and LSC (Np). After reaching equilibrium conditions, selected solid phases were characterized by XPS and XRD. Aqueous speciation was investigated by TRLFS and UV–vis/NIR for Cm(III) and Np(V), respectively.

A clear red-shift of the Cm(III) fluorescence peak with increasing borate concentrations indicate complex formation for $[B]_{tot} \geq 0.04$ M and $6 \leq pH_c \leq 9$. In spite of this, no significant increase in Nd(III) solubility occurred in any of the investigated systems in the presence of $[B]_{tot} \leq 0.4$ M, compared to borate-free systems. On the contrary, a significant decrease in Nd(III) concentration was observed at $pH_c \leq 9$ in NaCl and $MgCl_2$ systems with $[B]_{tot} \geq 0.16$ M. This observation, together with a clear change in the slope of the solubility curve and the further confirmation by XPS analyses confirms the transformation of $Nd(OH)_3$(am) into a so far unknown Nd(III)-borate solid phase. Similar Nd(III) solubility data and XPS spectra are obtained in undersaturation experiments conducted with the hydrothermally prepared phase $Nd[B_4O_{13}(OH)_4]$(cr). The observed formation of a An(III)–borate phase with lower solubility than the corresponding pure hydroxide constitutes a new and potentially relevant retention mechanism for An(III) under repository-relevant conditions. The solubility of $Th(OH)_4$(am) remains largely unaffected by borate within $7 \leq pH_c \leq 11$ in dilute to concentrated NaCl and $MgCl_2$ solutions. UV–vis /NIR of the supernatant solution in equilibrium with NpO_2OH(am,fresh) shows a clear red shift of the NpO_2^+ peak ($\lambda = 981$ nm) for $[B]_{tot} \geq 0.16$ M. Analogously with the Nd(III) case, a decrease in solubility accompanied with a change in the color of the Np(V) solid phase takes place in some of the samples with the highest borate concentration. Additional solubility experiments with $UO_3\cdot 2H_2O$(cr) and $Na_2U_2O_7\cdot 1.6H_2O$(cr) are currently on-going to complete the relevant oxidation states within the actinide series with the final aim of establishing robust upper solubility limits and evaluate possible transformation processes into less soluble, repository-relevant, borate-bearing actinide phases.

E-mail address: katja.hinz@kit.edu

Precipitation and solubility of calcium aminophosphonates

Rasha Hussein, Wolfgang Voigt

Institute of Inorganic Chemistry, TU Bergakademie Freiberg, 09596 Freiberg, Germany

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Abstract

Phosphonates are widely used in the industrial and household applications including cooling waters systems (water treatment), oil production and in medicine. In most of these applications either inhibition of adsorption or precipitation is proposed to be the primary mechanism of action.

The purpose of the present work is to study the precipitation and the solubility of calcium aminophosphonates at 25°C and ionic strength of 1 M NaCl. The phosphonates used were diethylenetriaminepentakis(methy1enephosphonic acid) DTPMP, Ethylenediaminetetrakis (methylenephosphonic acid) EDTMP, Nitrilotri(methy1enephosphonic acid) ATMP.

The precipitation of calcium phosphonate salts was performed under various conditions. With the precipitates of different types of calcium phosphonate salts were carried out solubility experiments. The equilibrated samples have been chemically analyzed and spectroscopic and diffractometric characterized to determine the chemical formula of these salts as $Ca_x \cdot L_y \cdot nH_2O$. According to these data and additional data for solution speciation it was possible to calculate the solubility products (K_{sp}) of the different calcium phosphonates.

E-mail address: wolfgang.voigt@chemie.tu-freiberg.de

Sodium magnesium selenate decahydrate, $Na_2Mg(SeO_4)_2 \cdot 10H_2O$, a new selenate salt

S. Kamburov,[1] H. Schmidt,[2] W. Voigt,[2] Chr. Balarew[1]

[1]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
[2]*Institute of Inorganic Chemistry, Technische Universität Freiberg, Germany*

Abstract

It is known that there exist certain similarities between the composition of the hydrates and the solubility diagrams of sulfate and selenate salts. Particularly salient are the similarities between sulfate and selenate double salts [1-3], which often are isostructural as well.

Solutions with magnesium selenate, sodium selenate and water were prepared and a nucleus of $Na_2Mg(SO_4)_2 \cdot 4H_2O$ was inserted. The solutions were laid in open petri dish at room temperature around 24-28°C. The obtained crystals consisted of the so far unknown double salt $Na_2Mg(SeO_4)_2 \cdot 10H_2O$.

The measurements on single-crystal X-ray diffractometer were conducted at 150 K.

The crystals are monoclinic P 1 21/a 1 (14), a=10.2710 Å, b=6.6100 Å, c=12.6720 Å, β=106.6400°, V=824.29 Å^3, Z=4.

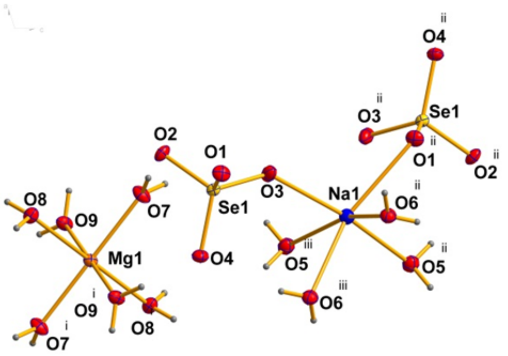

Figure 1

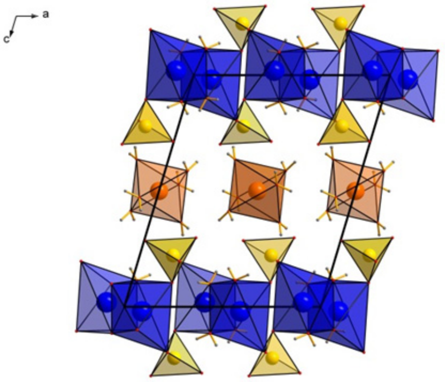

Figure 2

The compound is build up from isolated octahedra of $Mg(H_2O)_6$, Na coordinated by 4 water molecules and 2 oxygen atoms of SeO_4^{2-}. Mg1 is located on a center of symmetry (Fig. 1).

On Fig. 2 are shown the alternating layers of $[Mg(H_2O)]^{2+}$ octahedra and layers of water sharing chains of $[Na_2(SeO_4)_2(H_2O)_4]^{2-}$ octahedra. The water sharing chains are connected *via* selenate tetrahedra.

This double salt is isostructural to $Na_2Mg(SO_4)_2 \cdot 10H_2O$ described by Leduc *et al.*[4].

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E-mail address: s.kamburov@svr.igic.bas.bg

Temperature Dependence of the Solubility Product of Zirconium Hydroxide

T. Kobayashi,[1] T. Uemura,[1] T. Sasaki,[1] H. Moriyama[2]

[1]*Department of Nuclear Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku 615-8540, Kyoto, Japan*
[2]*Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun 590-0494, Osaka, Japan*

Abstract

The decay heat emission from the high level vitrified radioactive waste in the repository will be transferred to the groundwater aquifers through the surrounding engineered and geological barrier systems. In the early failure scenario of the waste package, the long-lived radionuclides including tetravalent actinides An(IV) leached in the groundwater are exposed to the elevated temperature environment up to 100°C. Though the solubility of An(IV) at 25ºC is generally controlled by the amorphous hydroxide as solubility-limiting solid phase and described using relevant thermodynamic constant [1], crystallization of Zr(IV) amorphous hydroxide as chemical analogues for An(IV) at 90ºC has been reported [2]. For the improvement of safety assessment of waste disposal, reliable predictions of the solubility limit of tetravalent radionuclides and the involved thermodynamic constants at the elevated temperature are indispensable. In the present study, solubility of zirconium hydroxide after aging at 5ºC to 60ºC range was measured at different temperatures to investigate the effects of crystallization of amorphous hydroxide and thermodynamic constants at elevated temperatures on the apparent solubility of zirconium hydroxide.

Sample solutions by oversaturation method were prepared by adding NaOH or $HClO_4$ to the acidic Zr perchlorate solutions ([Zr] = 0.01 mol/dm^3 (M)). The ionic strength (I) were adjusted to be $I = 0.5$ by adding appropriate amount of $NaClO_4$. After given periods at 5ºC, 40ºC and 60ºC, the sample solutions were taken from a temperature chamber. Then, pH values were measured keeping at 5 to 60ºC in a thermostat bath. After filtration of supernatants through the ultrafiltration membranes (3 kDa – 100 kDa NMWL) at respective temperatures, the apparent solubility of zirconium was determined by ICP-MS. XRD was used to characterize the crystallinity and the particle size of the solid phase.

The apparent solubility of filtrate after aging at 40ºC was slightly lower than those kept at 25ºC and this phenomenon would indicate the process of crystallization of amorphous hydroxide. The solubility products (K_{sp}) after aging were related to the particle size of the solid phases [3]. After aging at 40ºC, the solubility was also measured at 5 and 40ºC to compare the K_{sp} at different temperatures. Assuming no temperature dependence of enthalpy change ($\Delta_r H^o$), the $\Delta_r H^o$ was determined to be –101.4±8.7 kJ/mol for $Zr^{4+} + 4OH^- \Leftrightarrow Zr(OH)_4$ (s,40ºC), which was slightly higher than the $\Delta_r H^o$ (–133.6 kJ/mol) for $Zr(OH)_4$(am) calculated from the standard enthalpy of formation [4]. Similar analysis was performed for the solubility after aging at 5 and 60ºC, and temperature dependence of K_{sp} values were discussed.

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E-mail address: kobayashi@nucleng.kyoto-u.ac.jp

JESS solubility database: A versatile tool for the compilation and evaluation of solubility data

Erich Königsberger, Darren Rowland, Lan-Chi Königsberger,
Michael Hill, Peter May

Chemical and Metallurgical Engineering and Chemistry, Murdoch University, Murdoch, WA 6150, Australia

Abstract

The IUPAC Subcommittee on Solubility and Equilibrium Data has been selecting, editing and reviewing projects and manuscripts for publication as part of the IUPAC-NIST Solubility Data Series (SDS). This series provides comprehensive reviews of data from the primary literature for solubilities of gases, liquids and solids in liquids or solids. Data are compiled in a uniform format, critically evaluated and, where high-quality data from independent sources agree sufficiently, recommended values are proposed [1]. SDS Volume 102 was published recently [2].

A current IUPAC project is dealing with solubilities of substances related to urolithiasis [3]. Kidney stones consist of a range of inorganic and organic substances that are sparingly soluble in urine, thereby producing ionic and uncharged aqueous species which can undergo a wide variety of protonation and complexation reactions. Using these data as an example, this work explores the features of the JESS solubility database [4] that assist with the presentation, manipulation and critical evaluation of solubility data. In particular, the unique combination of databases available in JESS for speciation equilibria [5], physicochemical properties of solutions [6] and solubilities provides improved evaluation facilities, including the assessment of thermodynamic consistency among solubility, calorimetric and speciation data as described in a recent SDS volume [7]. Systems of different chemical complexity will highlight the benefits of applying the JESS software package to the production of future SDS volumes.

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E-mail address: E.Koenigsberger@murdoch.edu.au

Structure and spectroscopic properties of actinyl(VI)-nitrate complexes in the solid state and in aqueous nitric acid

Patric Lindqvist-Reis,[1] Christos Apostolidis,[2] Olaf Walter,[2] Rafał Janicki,[3] Remi Marsac,[1] Mikhail Yu. Skripkin,[4] Nidhu Lal Banik,[1] Jörg Rothe[1]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany
[2]European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany.
[3]University of Wrocław, Faculty of Chemistry, F. Joliot-Curie 14, 50-383 Wrocław, Poland.
[4]Department of Chemistry, St. Petersburg State University, Universitetsky pr., 26, 198904 St. Petersburg, Russia.

Abstract

Neptunium and plutonium are the two radioactive elements succeeding uranium in the actinide series. Although they are not primeval in nature, large quantities of the elements have been generated in the nuclear industry, plutonium as fuel, neptunium as byproduct. In the PUREX process, spent nuclear fuel is dissolved in nitric acid, followed by liquid-liquid extraction steps for separation and recovery of uranium and plutonium, while neptunium is discarded. In aqueous systems uranium usually occurs in its +6 state as an uranyl ion, UO_2^{2+}, while the main oxidation states of neptunium and plutonium strongly depend on the chemical environment. Although oxidation states from +3 to +7 are possible for neptunium and plutonium in aqueous solution, in the PUREX process solutions where the concentration of nitric acid is high, oxidation states of +4, +5, and +6 dominate. Despite that nitrate it is a weakly coordinating anion to metal ions in aqueous solution, at higher nitrate concentrations it forms inner-sphere complexes with hexavalent uranyl, neptunyl, and plutonyl. In the process solutions a fair amount of neptunyl- and plutonyl-nitrate complexes is therefore to be expected. Hence, basic knowledge about actinide speciation in aqueous nitrate solutions, including thermodynamic and structural characteristics, is necessary for optimization of such processes. Systematic experimental studies along the series of hexavalent actinides are also important to critically evaluate the concept of oxidation state analogy frequently used in actinide chemistry.

There are several spectroscopic studies published on uranyl-nitrate complexation in aqueous solution but relatively few on the corresponding hexavalent neptunium and plutonium systems.[1-6] Though, the agreement between the studies regarding the stoichiometry of the solution species at a given nitrate concentration is poor. For example, EXAFS studies showed that UO_2^{2+} and NpO_2^{2+} were coordinated by three and two nitrate ions, respectively in 15 M HNO_3,[1-2] while vis-NIR absorption and Raman studies showed that one nitrate ion was bound to PuO_2^{2+} in 15 M HNO_3.[3] These results are in variance with two earlier vis-NIR absorption spectroscopic studies on NpO_2^{2+} and PuO_2^{2+} in nitric acid,[4-5] where it was concluded that the major complex in 15 M HNO_3 was a dinitrate complex. In a recent paper on neptunyl(VI) ions in aqueous HNO_3 solutions we showed that the dinitrate complex mainly occurs in concentrated nitric acid.[6] Here, we present crystal structures, optical absorption and vibrational spectra of $[An^{VI}O_2(NO_3)_2(H_2O)_2]\cdot H_2O$ (An = U, Np, Pu; x = 0, 1, 4), together with relevant spectroscopic data on the An(VI) ions in aqueous solution at high nitric acid concentration. An important question is whether the complexes present in the crystals also occur in solution. We thus compared the spectroscopic data of the above-mentioned compounds with those of the corresponding aqueous solutions, which we measured at HNO_3 concentrations ranging from 0 to 14 M. Depending on the acid concentration, different distributions of hydrated AnO_2^{2+}, $[AnO_2(NO_3)]^+$ and $[AnO_2(NO_3)_2]$ species were established.[6] In contrast to previous work,[3-5] small redshifts relative to the spectra of the non-complexed ions were observed in both the vis-NIR absorption spectra of the Np(VI) and Pu(VI) solutions between 4 and 10 M HNO_3. We explain these shifts as being due to a likewise small increase in the ion's ligand-fields upon formation of a mononitrate complex. The large blue-shifts appearing above 10 M nitric acid are thus consistent with the formation of dinitrate complexes with weaker ligand fields than the mononitrate complexes, in agreement with the absorption spectra of $[AnO_2(NO_3)_2(H_2O)_2]\cdot H_2O$. Our assignment of the bands due to mono- and dinitrate complexes differs from those of earlier investigators.[3-5]

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E-mail address: patric.lindqvist@kit.edu

THEREDA Database Project: Data Selections for Actinides

Christian M. Marquardt, Xavier Gaona, Vanessa Montoya, Marcus Altmaier

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

Abstract

THEREDA is a German **the**rmodynamic **re**ference **da**tabank project that, besides developing the technical platform for data management, compiles, evaluates and selects reliable thermodynamic data for use in long-term safety analyses of geological waste repositories. The criteria for the compilation of data strongly relates to research in the frame of final disposal of radioactive waste in Germany. Hence, the database considers the geochemical conditions of crystalline rock, salt, and clay stone formations. In THEREDA, the Pitzer- and SIT-formalisms to describe activity coefficients of hydrated ions and molecules are supported. Regarding the potential temperature range in the repository, geochemical modeling has to cover temperatures up to 150 °C. At present, THEREDA focusses on Pitzer consistent thermodynamic data.

THEREDA was started in 2006 as a consortium of key institutions working on safety research for nuclear waste disposal in Germany:

- GRS - Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Braunschweig
- HZDR - Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology
- KIT-INE - Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal
- TU Bergakademie Freiberg, Institute of Inorganic Chemistry
- AF-Consult Switzerland AG, Baden (Switzerland).

Within the THEREDA consortium, the Institute for Nuclear Waste Disposal (INE) at KIT is responsible for the thermodynamic data of actinides and selected fission products. For more information on the data selection and THEREDA, please visit the project webpage at www.thereda.de. THEREDA releases include data selections by KIT-INE on actinides:

2. Release: system Na, Mg, Ca – Cl^- - Am(III), Nd(III), Cm(III) - $H_2O(l)$
4. Release: system Na – Cl^- - Np(V)
7. Release: system Na - K - Ca - Cl^- - Th(IV) - Np(IV) - Pu(IV) - C (25°C)
8. Release: system Na, Mg, Ca, Cl^-, SO_4^{2-}, CO_3^{2-} - Am(III), Cm(III) - $H_2O(l)$ (25°C)

Release No. 1 and 3 of THEREDA includes data on the oceanic salt system (selected by TU Freiberg). Release No. 5 and 6 consider the element Cs (selected by GRS Braunschweig) and the cement system (selected by AF-Consult Switzerland), respectively. Uranium will be addressed in an upcoming release in 2014 (data selected by HZDR). All THEREDA releases are internally consistent. Data can be downloaded by registered users via the project webpage. For external users, data have been released as parameter input files for the geochemical codes EQ3/6, Phreeqc, Geochemists Workbench, and ChemApp.

E-mail address: christian.marquardt@kit.edu

Cellulose solubilisation in biodegradable mixtures of short-chain quaternary ammonium carboxylate ionic liquids (qacils) and “green” co-solvent

Andrea Mühlbauer,[1,2,3] Loïc Leclercq,[1] Werner Kunz,[2] Sinisa Marinkovic,[3]
Boris Estrine,[3] Véronique Nardello-Rataj[1]

[1]Université Lille 1, Chimie Moléculaire et Formulation, 59655 Villeneuve-d'Ascq, France
[2]Universität Regensburg, Physical and Theoretical Chemistry, 93040 Regensburg, Germany
[3]Agro-Industrie Recherches et Développement, 51110 Pomacle, France

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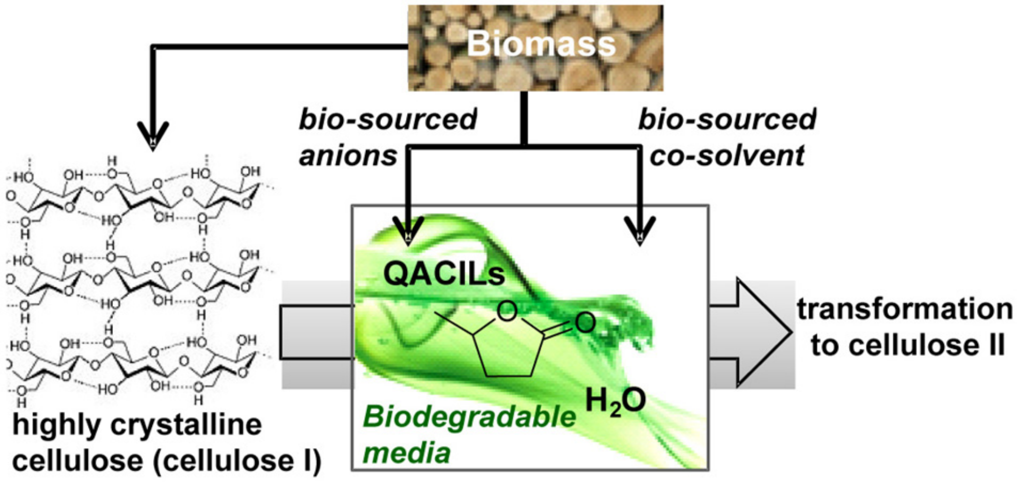
Abstract

Around fifty two- and three-tailed short chain quaternary ammonium combined with various organic carboxylate counter-anions have been prepared and studied. Their physicochemical properties as well as their ionic liquid (IL) behavior have been investigated and rationalized according to the structural parameters of both ions. Apart from thermal transitions which were investigated by differential scanning calorimetry, the viscosities and the surface activities of the different amphiphilic salts have been determined showing that those physicochemical properties are not only influenced by the chain length of the cation but also by the structure of the counter-anion.

These QACILs have been tested for the dissolution of cellulose showing a successful effect of the natural organic anion, in particular acetate, levulinate and itaconate. Particularly, the combination of levulinate as a renewably sourced anion with short chain alkyl ammonium as a cation are able to dissolve up to 10 wt% of microcrystalline cellulose. During this solubilization, the crystalline structure of cellulose is transformed from cellulose I to cellulose II. Additionally, a high tolerance of water was found for such ILs (presence of up to 18 wt% of water). Hence technical grade ILs can be used, thus avoiding the energy-consuming drying process generally required with traditional ILs before dissolution experiments. In addition, co-solvents have been studied to optimize the dissolution process and the viscosity of the mixture. With 20 wt% of γ-valerolactone, a renewably-sourced co-solvent, the cellulose dissolution was improved up to 20 wt%, by the way the sustainability of the media is advanced.



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E-mail address: andrea.muehlbauer@ed.univ-lille1.fr; veronique.rataj@univ-lille1.fr

Modelling Iodine-groundwater-rock interaction with PHREEQC depending on depth

Esra Orucoglu,[1] Joonhong Ahn[2]

[1]*Faculty of Mines, Istanbul Technical University, TR-34469 Maslak, Istanbul, Turkey.*
[2]*Dep. of Nuclear Engineering, University of California at Berkeley, CA 94720-1730, USA*

Abstract

Transport of radionuclides through the geologic formation and their reactions with host rock and groundwater basically depend on their chemical forms. In numerous studies, iodine is recognized as one of the most important radionuclides that determine performance of geological disposal of radioactive waste for its bioavailability, mobility in soil, volatility, long-lived radioactivity and high fission yield [1, 2]. Its movement from a disposal site to earth surface should be delayed as much as possible. This could be achieved by being buried it much deeper than usual disposal sites and/or by sequestrating iodine isotopes in a highly robust waste form. As going deeper and deeper, the environmental conditions change and these variations affect the iodine speciation and thus movement. The variation in the system, like pH, redox potential and temperature, affects the iodine speciation and the interaction between iodine, host rock and groundwater [3]. All of them lead to complicated interactions that should be identified to better assess the iodine speciation and migration in the radioactive waste disposal system. Iodine shows complex geochemical behavior and its chemical speciation determine its transport in aqueous environments [4]. For this reason iodine speciation should be modeled as a first step. Geochemical modeling techniques are helpful tools to identify these types of complex interactions and they are part of the performance assessment studies for radioactive waste disposal investigations.

In this study, it is aimed to simulate iodine speciation in aqueous environment by using PHREEQC code. After simulating depth dependent groundwater evolution, iodine speciation and iodine sorption reactions, interaction between iodine groundwater and host rock are modeled based on equilibrium concept and obtained depth dependent sorption distribution coefficients (K_d) are used in TTBX code for iodine transport. The code is developed by van den Akker and Ahn [5]. The effect of sorption in iodine migration is investigated in the TTBX code by comparing with and without sorption. From geochemical simulation results, it is found that the I^- is the only specie in system and depth dependent K_d values are in the range of $1.12 \times 10^{-6} – 1.57 \times 10^{-5}$ kg/m^3 for rock matrix and are in the range of 8.35×10^{-7} – 9.98×10^{-6} for fracture filling minerals within 100-1000 m depth interval in crystalline rock. The TTBX simulation results figure out that although the Kd values are very low, sorption slows down the iodine migration. The results obtained from this study could form a basis for radioactive waste disposal researches considering iodine interaction with groundwater and rock minerals.

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E-mail address: orucoglu@itu.edu.tr

TRLFS study of the UO_2^{2+} - SO_4^{2-} - H_2O system: Analysis of the factors that may lead to misinterpretation of U(VI) speciation

V.G. Petrov, E.A. Shirshin, G.S. Budylin, E.A. Enina, V.V. Fadeev, S.N. Kalmykov

Lomonosov Moscow State University, 119991, Leninskie gory, 1/3, Moscow, Russia

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Abstract

The aqueous chemistry of uranium(VI) determines its migration in geosphere under oxic conditions. Time-resolved laser fluorescence spectroscopy (TRLFS) is a powerful method to determine U(VI) speciation in solutions and at mineral-water interfaces [1]. This method allows spectral and temporal selection of different uranium(VI) species and implies measurement of fluorescence decay curves on a microsecond timescale. Due to its high sensitivity and selectivity TRLFS is extensively used by many research groups for determination of U(VI) complex formation constants and monitoring U(VI) speciation in drainage and natural waters. But it was shown that there are some discrepancies in excited state lifetime values for certain uranyl complexes obtained by different groups [2]. Moreover, even the number of components required for fluorescence decay curves fitting is not clear: some researchers consider discreet lifetimes for different complexes, while others postulate a continuous dependency of lifetime on ligand concentration and interpret their data under the assumption of fast ligand exchange.

Here, we'll present the extensive study of the reasons that may lead to the discrepancies of photophysical parameters obtained for the certain uranium(VI) complexes. First, we have demonstrated recently that the effect of excited states annihilation may influence the shape of fluorescence decay curves at high excitation intensities resulting in misinterpretation of fluorescence decay rates. For typical parameters of laser radiation used in TRLFS experiments (wavelength 266 nm, mJ pulse energy, nanosecond pulse duration, mm beam radius) it can be estimated that the fraction of excited complexes in the irradiation volume is close to unity and the diffusion on microsecond timescale can lead to collisional bimolecular quenching, thus resulting in the increase of fluorescence decay rate [3]. Therefore, this effect can lead to false fluorescence decay parameters and should be taken into account when determining U(VI) speciation by TRLFS. Second, different algorithms of fluorescence decay curves processing (the use of fixed lifetimes, global analysis etc.) may provide different values of complexes amplitudes and, consequently, equilibrium constants. Third, we'll demonstrate the influence of ionic strength on U(VI) complexes photophysical parameters and stoichiometry by the example of uranyl sulfate complexes. At the last, we present the equilibrium constants for uranium(VI)-sulfate complexes formation obtained with taking all the aforementioned facts into account.

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E-mail address: vladimir.g.petrov@gmail.com

Nanocrystaline cerium dioxide solubility determined by radioactive tracers technique

T.V. Plakhova,[1] A.Yu. Romanchuk,[1] V.K. Ivanov,[2] D. Shuh,[3] S.N. Kalmykov[1]

[1]*Lomonosov Moscow State University, Moscow, Russia*
[2]*Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia*
[3]*Lawrence Berkeley National Laboratory, USA*

Abstract

Nanosized ceria is one of the most promising rare earth oxides with many attractive properties that make it highly perspective in the wide range of applications from gas sensors and electrode materials to therapeutic agent for treating a number of diseases. Ceria nanoparticles exhibit a good chemical and thermal stability and excellent biological compatibility. However, there is still a lack of knowledge on CeO_2 solubility in aqueous solutions, Ce^{3+}/Ce^{4+} surface ratio and related size-dependent properties.

The present study is aimed to determine the solubility of cerium dioxide nanoparticles using radioactive ^{141}Ce marker and to study Ce^{3+}/Ce^{4+} ratio on the surface of nanoparticles and in the solution.

Synthesis of ceria nanoparticles with radioactive tracer was carried out by adding aqueous ammonia to cerium (III) nitrate stock solution containing ^{141}Ce. The precipitate was washed with deionized water and split to several portions for solubility study as a function of pH. Part of the samples was placed in nitrogen glovebox to prevent CO_2 absorption.

The size and morphology of the nanoparticles was determined using high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The ζ-potential of nanoparticles suspension was measured by dynamic light scattering. X-ray absorption spectroscopy using Ce $M_{4,5}$ - and O K-edges was used to determine Ce(III)/Ce(IV) ratio on the surface and in the bulk of ceria nanoparticles. The solubility was determined by measuring ^{141}Ce by γ-spectroscopy in the solution equilibrated with ceria.

According to HRTEM data ultrafine CeO_2 nanoparticles with fluorite crystal structure were obtained. A strong correlation between concentration of Ce(III) nitrate precursor solution and ceria nanoparticle size was observed. CeO_2 suspension stability in aqueous solutions was observed at pH<5 and pH> 7.5; the pH_{IEP} was established as 6.5. No correlation between nanoparticles size and suspension stability was observed. The well pronounced difference in XAS spectra for 2 nm and 5 nm ceria particles was established that could be explained by increase of Ce(III) on the surface upon the decrease of the particle size.

CeO_2 solubility experiments were performed under equilibrium conditions for 2 nm and 5 nm nanoparticles in the range of pH from 2 to 12. Upon the increase of pH the significant decrease in solubility was observed (from 10^{-5} M at pH=2 to 10^{-7} M at pH=8), in the range from pH=8 to pH=12 the solubility remained unchanged. The effect of carbonates presence on the nanocrystalline CeO_{2-x} solubility was discussed. Reductive dissolution model was proposed for experimental data fitting: $CeO_2 + e^- + 4H^+ \leftrightarrows Ce^{3+} + 2H_2O$.

E-mail address: tatiana.v.plakhova@gmail.com

A quantum chemical study on Tc(IV) hydrolysis species and ternary Ca-Tc^{IV}-OH complexes in alkaline $CaCl_2$ solutions

Robert Polly, Bernd Schimmelpfennig, Ezgi Yalcintas, Xavier Gaona, Marcus Altmaier

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

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Abstract

Tc-99 is a redox-sensitive β-emitting fission product with very long half-life ($t_{½}$ ~211.000 a). Tetravalent Tc(IV) exists under very reducing conditions like expected for operative deep geological nuclear waste repositories. Tc(IV) hydrolizes very strongly. The anionic species $TcO(OH)_3^-$ is known to dominate the aqueous chemistry of Tc(IV) at high pH conditions. In concentrated alkaline $CaCl_2$ solutions, comprehensive solubility studies performed by E. Yalcintas of KIT-INE recently established the hitherto unknown formation of higher hydrolysis species of the type $Ca_x[TcO(OH)_y]^{2+2x-y}$.

Quantum chemical calculations are well suited to analyse Tc(IV) solvation processes. However, so far there are no ab initio calculations on $[TcO]^{2+}$ or Tc(IV) hydrolysis species, but only on TcO [1] and Density functional theory (DFT) calculations on $[TcO]^{2+}$ [2]. In the present work we performed pilot studies on these species with high level Complete Active Space Self Consistent Field (CASSCF) and Multi Reference Configuration Interaction (MRCI) calculations to determine the character of the ground states of these species. The calculations were carried out with MOLPRO and TURBOMOLE.

Our calculations using advanced quantum chemical tools show for the first time that the ground states of the species, $[TcO]^{2+}$, $[TcO(OH)_y]^{2-y}$ and $Ca_x[TcO(OH)_y]^{2+2x-y}$ are single reference states and therefore the application of DFT calculations is permitted in this case. This will enable us to further apply large DFT calculations and determine the structure of relevant Tc(IV) species in alkaline solutions involving a large number of water molecules and solvated ions in more detail.

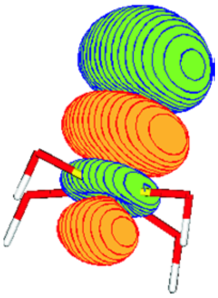

Figure 1 *Bonding σ orbital in $[TcO(OH)_4]^{-2}$*

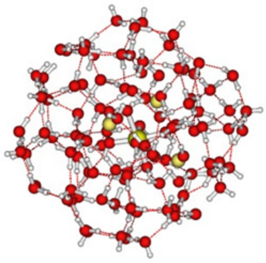

Figure 2 *$Ca_3[TcO(OH)_5]^{3+}$ complex embedded in 100 water molecules*

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E-mail address: robert.polly@kit.edu

Release of Fission Products and Actinides from Simulated Nuclear Oxide Fuel under Supercritical Water Nuclear Reactor Conditions

L. Qiu, D. Guzonas, S. Livingstone, S. Rousseau

Atomic Energy of Canada Limited, 1 Plant Road, Chalk River, Ontario, Canada K0J 1J0

Abstract

The release of fission products and actinides into the coolant after a fuel defect and their transport to out-of-core surfaces is a concern for all water-cooled nuclear reactors, including future supercritical water-cooled reactor (SCWR) concepts. High temperature solubility data are fundamental inputs for any model of activity transport in a SCWR. The Canadian SCWR concept will operate at 25 MPa with core inlet and outlet temperatures of 350 and 625 °C, respectively. The physical and chemical properties of water change drastically at the transition from the subcritical to supercritical regions, and while the solubilities of many inorganic species of interest decrease rapidly with increasing temperature, the solubilities of others increase with increasing temperature and some, such as UO_2, show little dependence on temperature. There are little or no high temperature solubility data for many of the compounds of interests, especially in the supercritical region. Furthermore, current theoretical models cannot reliably predict solubilities in supercritical water (SCW) as many parameters in these models are derived by extrapolation of data obtained at much lower temperatures. It is therefore difficult to develop models of activity transport for an SCWR. This paper will present the results of recent dissolution measurements for a uranium-thorium simulated nuclear oxide fuel under SCWR chemistry conditions and discuss the results based on the known solubility data for relevant oxides under similar conditions. The potential implications for activity transport in an SCWR will also be discussed.

E-mail address: qiul@aecl.ca

Leaching behavior of intrinsic colloids and pseudocolloids of plutonium

A.Yu. Romanchuk,[1] A.V. Egorov,[1] Y.V. Zubavichus, [2] S.N. Kalmykov[1]

[1]Lomonosov Moscow State University, Leninskie gory, 1 bld.3, 119991, Moscow, Russia
[2]National Research Centre "Kurchatov Institute", Akademika Kurchatova pl. 1., 123182, Moscow, Russia

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Abstract

Plutonium is the chemical element of the major concern at the nuclear legacy sites in USA and former Soviet Union. It was previously shown that plutonium can migrate in the subsurface environment with colloidal fraction. Colloidal migration of plutonium can be defined by the formation of pseudocolloids when plutonium is sorbed onto various colloidal particles or formation of intrinsic colloids. Additionally it was shown that depending on the experimental conditions plutonium can form surface precipitates on various mineral colloids. Depending on the speciation, plutonium demonstrates different leaching behavior and desorption from colloids. In this paper we aimed to develop a simple leaching test to study the difference in plutonium speciation.

Leaching behavior of plutonium sorbed onto mineral (hematite, magnetite, anatase) and intrinsic plutonium colloids is studied. Leaching tests were done by adding aliquot of diluted perchloric acid to make pH 1.3. Then plutonium concentration in solution was measured as a function of time . Intrinsic plutonium colloids were synthesized by adding NaOH solution to Pu(IV) solution. HRTEM and XAFS were used to characterize these colloids.

To prepare pseudocolloids, Pu(VI) was interacted with mineral suspension at different total radionuclide concentration. It was previously shown that speciation of plutonium onto hematite surface is depend on its concentration: at low concentration Pu(IV) is chemisorbed while at concentration $>10^{-10}$ M crystalline $PuO_{2+x}\cdot nH_2O$ nanoparticles are formed [1].

It is shown that leaching behavior of chemisorbed Pu(IV) species is different from leaching behavior plutonium intrinsic colloids. It is a powerful technique for determination of Pu speciation onto solid surface in wide range of plutonium total concentrations including tracer concentrations. It was found that leaching behavior is in the complete agreement with plutonium speciation which was determined by XAFS and HRTEM.

It is also was found that increasing of the sorption equilibration time result in slow leaching of plutonium from the surface. It can be explained by aging of $PuO_{2+x}\cdot nH_2O$ colloids onto mineral surface with time.

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E-mail address: romanchuk.anna@gmail.com

Experimental study of solubility and liquid-liquid equilibria in quaternary reactive system acetic acid – *n*-butanol – *n*-butyl acetate – water

A.A. Samarov, M.A. Toikka, A.M. Toikka

Saint Petersburg State University, Department of Chemical Thermodynamics and Kinetics, 198504,
Saint-Petersburg, Peterhof, Universitetskiy pr. 26, Russia

Abstract

The studies of solubility and liquid-liquid equilibrium (LLE) are of well-known importance for basic physical-chemical research. The object of presented study is a system with n-butyl acetate synthesis reaction. The reagents and products of this reaction constituent the acetic acid – n-butanol – n-butyl acetate – water system. Due to the area of immiscibility in this system the process of ester synthesis could be accompanied by the splitting of solution. This phenomenon may lead to some additional peculiarities in the run of reaction. In the industrial design of ester synthesis it would be desirable to avoid the liquid-liquid envelope. Accordingly the knowledge of solubility and LLE data is important for the optimization of ester synthesis. Liquid phase splitting in reacting systems is relevant also for basic thermodynamic analysis. In spite of numerous research on LLE in the systems with ester synthesis reaction the data sets on the acetic acid – n-butanol – n-butyl acetate – water systems including ternary and binary sub-systems are relatively limited and incomplete. This work is a continuation of the studies of thermodynamic properties of multicomponent systems with coupled mass transfer and chemical reaction [1-4].

The experimental study of solubility and LLE was carried out at 308.15 K. The compositions of coexistent phases (LLE) were determined by gas chromatographic analysis (Cristal 5000, Chromatec, Russia). The cloud-point technique was applied in the study of the vicinity of critical states of LLE. The experimental data on the organic and aqueous phases were obtained for quaternary system and three ternary subsystems (acetic acid – n-butyl acetate – water, n-propanol – n-butyl acetate – water and acetic acid – n-butanol – water systems). The accuracy of composition determination does not exceed ±0.005 mole fraction of the component. On the base of experimental LLE data we determined the mutual disposition of stoichiometric lines and liquid-liquid envelope in composition tetrahedron. These results provide the opportunity to estimate the possibility of the splitting of reaction solution in the run of ester synthesis and ester hydrolysis.

The NRTL model was used to calculate LLE and to correlate the experimental data. The comparison of LLE data with the values calculated from NRTL models indicates that the experimental and calculated data are in sufficient agreement. In the results of the study we obtained the complete topological structure of the liquid phase diagram of acetic acid – n-butanol – n-butyl acetate – water system.

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E-mail address: samarov@yandex.ru

Solubility and hydrolysis of NpO_2(am) and PuO_2(am) in dilute to concentrated NaCl solutions

J. Schepperle, D. Fellhauer, X. Gaona, M. Altmaier, H. Geckeis

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

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Abstract

The reliable long-term safety assessment of nuclear waste disposal requires the analysis of possible future events that can impact the safety of a disposal site. In the case of water intrusion into a repository the release of radionuclides from the corroding waste forms and the formation of aqueous radionuclide systems in the near-field of the containers has to be analysed. In order to assess the risk of a potential migration of radionuclides into the far-field and, finally, into the biosphere, a thorough understanding and thermodynamic description of the basic geochemical processes of radionuclides in aqueous solutions is mandatory. Several processes related to solubility, complexation, sorption, colloid formation, etc. have to be studied and quantified.

Although the solubility and hydrolysis behavior of NpO_2(am) and PuO_2(am) was subject of several studies, some questions remain open for these systems:

- solubility data for NpO2(am) and PuO2(am) are missing for $3 \leq pHc \leq 6$, thus hindering the accurate description of Np(IV) and Pu(IV) hydrolysis in this pH region;
- almost all available solubility data for NpO2(am) and $pHc > 6$ are reported with large uncertainty or are but upper limit values (detection limit of the determination method);
- comprehensive solubility studies with NpO2(am) and PuO2(am) covering a wide range of background electrolyte concentrations and pHc values are not available.

In the present work, the solubility of NpO_2(am) and PuO_2(am) in dilute to concentrated NaCl brines (0.1, 0.5, 2.0, 4.0 and 5.0 M) at $pH_c = 2 – 13$ is investigated. NpO_2(am) was precipitated with NaOH from an electrochemically prepared oxidation state pure Np(IV) stock solution. Batch solubility samples contained approx. 1 – 3 mg of NpO_2(am) in 30 mL of the corresponding pH_c adjusted NaCl / NaOH / HCl matrix solutions. Millimolar amounts of the reducing agents Sn(II), $Na_2S_2O_4$ or AH_2QDS were added to stabilize the tetravalent oxidation state. Redox-inert pH buffers (MES, PIPES,…) were used to adjust pH_c conditions in the near-neutral pH range 5 to 9. The results (determination of [Np(IV)] by liquid scintillation counting LSC) are compared to thermodynamic model calculations based on the specific ion interaction theory (SIT) [1] and the available data from NEA-TDB and Neck *et al.* [2,3].

For $pH_c < 5$, measured Np(IV) concentrations in 0.1 to 2.0 M NaCl are in very good agreement with the SIT modeled solubility curves, whereas slightly lower experimental values are found in 4.0 and 5.0 M NaCl. For $pH_c > 5$, [Np(IV)] are at LSC detection limit ($\approx 5 \cdot 10^{-9}$ M) independently of the NaCl concentration. Although the obtained values do not contradict the expected behavior, no further information can be obtained from the data at present. Quantification of [Np(IV)] in these low concentration level samples by (HR)ICP-MS is under way. A detailed thermodynamic evaluation based on both the SIT and Pitzer approach will follow at the end of the experimental work.

Analogue experiments with PuO_2(am) are in preparation. In a first step, Pu(IV) in 1 M $HClO_4$ was electrochemically oxidized to Pu(VI) followed by a reduction to PuO_2(am) with hydroquinone at pH ≈ 8 (pe ≈ 0.4) within few days. This in-situ reductive precipitation method ensures a rather slow crystallization compared to the standard approach (rapid precipitation of PuO_2(am) from an acidic Pu^{4+} solutions with NaOH leading to massive supersaturation and likely changes of the initial Pu oxidation state). The adopted approach leads to significantly sharper peaks of the powder XRD pattern compared to PuO_2(am) prepared from strong supersaturation. As for Np(IV), this part of the work aims at deriving comprehensive chemical, thermodynamic and activity models for Pu(IV) hydrolysis and solubility in dilute to concentrated NaCl solutions.

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E-mail address: julian.schepperle@kit.edu

Phase equilibria in the fullerenol-containing systems

Konstantin N. Semenov,[1] Nikolay A. Charykov,[2] Igor V. Murin[1]

[1]Saint-Petersburg State University, Institute of Chemistry, 198504, Saint-Petersburg, Universitetskii pr. 26, Russia
[2]Saint-Petersburg State Technological Institute (Technical University), Saint-Petersburg, Moskovskii pr. 26, Russia

Abstract

Light fullerenes (C_{60} and C_{70}) can be applied in various areas of science and engineering, namely in materials science, mechanics, mechanical engineering, construction, electronics, optics, medicine, pharmacology, food and cosmetic industry, et al.[1,2] However the light fullerenes application is limited due to incompatibility of fullerenes with water and water solutions. For example, solubility of C_{60} in water at 25 °C according to ref. 1 is equal to 1.3×10^{-11} $g\cdot l^{-1}$, solubility of C_{70} is equal to 1.1×10^{-13} $g\cdot l^{-1}$.[1] The most part of the light fullerenes derivatives (fluoro, chloro, bromo, iodo, amino, carboxo, et al.) are also practically insoluble in water and water solutions, meanwhile they can be extensively applied in mechanical engineering (in water-soluble freezing and antifriction compositions), construction (as a soluble additives to cements and concretes), medicine and pharmacology (due to compatibility with water, physiological solutions, lymph, blood, digestive juices et al.), cosmetology (in the case of using of water and water- alcohol solutions).[1,2]

It should be pointed that: (i)currently the term "fullerenol" includes not only the fullerenols $C_{60}(OH)_X$, which are the derivatives of the fullerene C_{60} (the most easily accessible from all of fullerenes), but also hydroxyl- derivatives other individual fullerenes $C_n(OH)_X$ (n = 60, 70, 76, 78, 84, 90).; (ii) besides the hydroxyl groups, fullerenols can also include some other non-hydroxylic groups, such as oxygen groups (=O, -O-) $C_n(OH)_XO_Y$ and salt type groups, such as $[C_n(OH)_XO_Y](ONa)_Z$, etc.; (iii) finally, to fullerenol are referred mixtures of individual fullerenol of different composition or individual fullerenols of low purity (for example, less than 95 wt.%).[2,3]

Such physico - chemical properties of water solutions as concentration dependence of density, average molar and partial volumes of the solution components, concentration dependence of the refractive index, concentration dependence of the hydrogen ion concentration, dissociation constant, apparent degree of dissociation, specific conductivity, molar conductivity, average size of the fullerenol associates and the concentration dependence of the ς-potential were determined. Solubility diagrams in ternary systems fullerenol - NaCl - H_2O, fullerenol - Pr $(NO_3)_3$ - H_2O, fullerenol - YCl_3 - H_2O, fullerenol –UO_2SO_4 – H_2O, and fullerenol -$CuCl_2$ - H_2O at 25 ° C by the isothermal saturation method.[3]

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E-mail address: semenov1986@yandex.ru

Dissolution of Thorium Oxide in Aqueous Media

M. Simonnet, N. Barré, R. Drot, C. Le Naour, V. Sladkov, S. Delpech

Institut de Physique Nucléaire d'Orsay, 15 rue Georges Clémenceau, 91400 Orsay, France

Abstract

Because of rising energy demand and limited energy resources, new fuels need to be developed. In the nuclear field, thorium has recently been reinvestigated as a possible alternative to uranium solid fuel. It though needs further research, particularly in the reprocessing process called THOREX, which is very similar to the currently used process for uranium and plutonium treatment. This kind of reprocessing is done by fuel dissolution followed by liquid/liquid extraction in TBP-dodecane. Still, unlike uranium, thorium oxide is hardly soluble, even in very acidic solutions (10M to 15M). To achieve total dissolution, small amounts of hydrofluoric acid (0,03M to 0,1M) are added to concentrated nitric acid in the THOREX process. This leads to increased corrosion yields and requires a long time of batch dissolution (more than 10h). The aim of this study is thus to find a way to replace or reduce the amount of hydrofluoric acid with increasing dissolution rate.

Different media of dissolution are chosen according to literature data. A mixture of strong acid and complexing reagent is required to completely dissolve thorium oxide. Nitric acid and sulfuric acid are chosen as strong acids; oxalic acid and hydrofluoric acid as complexing reagents.

Two different stirring techniques have been used: mechanical stirring with a 3D stirrer called "turbula" or with a heating magnetic stirrer, and ultrasound stirring. The use of power ultrasound to improve chemical reactions is known as sonochemistry. When sound waves enter a solution, particles inside the medium move with the sinusoidal wave, creating empty and crowded areas. This leads to a pressure gradient. If enough power is given to the ultrasound waves, the pressure force can tear the liquid apart and creates a cavity. This cavity (or bubble), empty (or filled with vapor), will then grow up by following rarefaction/compression cycles. The bubbles finally reach the stability limit size and collapse. When collapsing, a huge energy is locally (10µm-100µm) given to the medium, with temperature as high as 5000°C and pressure around 200atm to 500atm in water. Mechanical and chemical effects of these extreme local conditions then help chemical reactions to happen.

Experiments were conducted in four main steps: synthesis of the ThO_2 by oxalates precursors, characterization of the solid powder by X-ray diffraction, dissolution of the thorium powder in a given media by using the physical techniques described above, and supernatant analysis by UV/Vis spectroscopy with Arsenazo III coloring complexing reagent, PERALS method and/or ICP/AES to get thorium concentration.

Results show that temperature drastically increases the dissolution rate. Sonochemistry also allows to reach total dissolution in few hours with HF concentration as low as 1mM, whereas only few percent of the initial thorium dioxide is dissolved with mechanical stirring at this concentration. The study now focuses on finding the ThO_2 dissolution mechanisms with both mechanical and ultrasound stirring, and on optimizing the main parameters: concentrations, ultrasound power, temperature and mass/volume ratio.

E-mail address: simonnet@ipno.in2p3.fr

The importance of the dissolved $Ca(OH)_2$ in hyperalkaline aqueous solutions

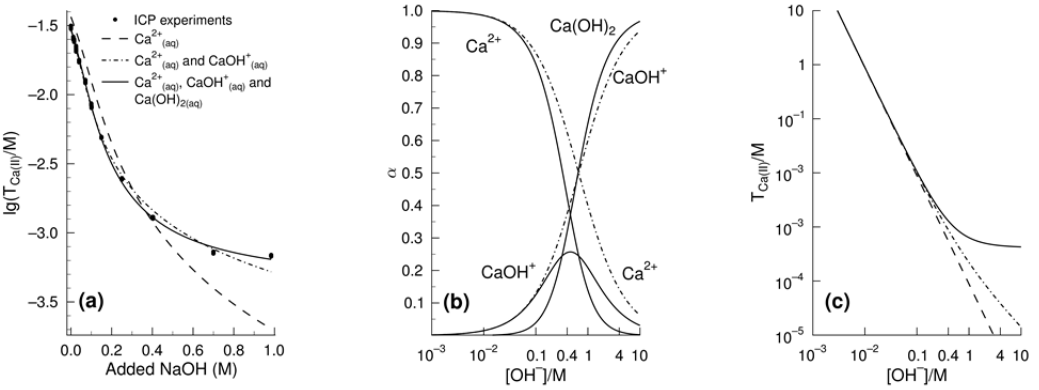
Attila Pallagi,[1,2] Gábor Peintler,[2,3] Attila Gácsi,[1,2] Bence Kutus,[1,2]
István Pálinkó,[2,4] Pál Sipos[1,2]

[1] *Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Dóm tér 7, Hungary*
[2] *Material and Solution Structure Research Group, University of Szeged*
[3] *Department of Physical Chemistry and Material Science, Univ. of Szeged, H-6720 Rerrich tér 1, Hungary*
[4] *Department of Organic Chemistry, University of Szeged, H-6720 Dóm tér 8, Hungary*

Abstract

The heterogeneous equilibrium of the solutions saturated with $Ca(OH)_2$ has been investigated many times for a long time. In spite of the considerable efforts, there are still uncertainties about the existing dissolved species. It has been known since 1923 [1] that the $CaOH^+$ exists in significant concentration, however, there is disagreement in the literature about the presence of the dissolved $Ca(OH)_2$. The aim of this work was to clarify the distribution of the existing Ca(II)-containing species in hyperalkaline solutions.

To clarify the role of $Ca(OH)_2(aq)$, NaOH solutions saturated with solid CaO were investigated in the concentration ranges of 0–1 M (ICP) and 0–4 M NaOH (precipitation titration, Ca-ISE), between 5 and 75 ºC. The ICP measurements, as well as, their evaluations are shown in the Figure at 25 ºC. Part (a) illustrates that the Ca^{2+}, $CaOH^+$ and $Ca(OH)_2(aq)$ species are able to describe the experiments together only, with the following coefficients: $L(Ca(OH)_2) = 8{,}8 \cdot 10^{-5}$ is the solubility product and $\beta_1(CaOH^+) = 1{,}5$ and $\beta_2(Ca(OH)_2) = 4{,}8$ are the stability products. The results were confirmed by Ca-ISE measurements and precipitation titrations.



The distribution diagram (b) shows clearly that the dissolved $Ca(OH)_2$ cannot be omitted above the concentration of ~0,2 M NaOH. Moreover, the dissolved $Ca(OH)_2$ becomes the most important species above the 2 M base concentration. One of its consequences is that the total Ca(II) concentration cannot be decreased below $\sim 3 \cdot 10^{-4}$ M by increasing the base concentration.

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E-mail address: sipos@chem.u-szeged.hu

Solubility data of lithium sulfate in binary and higher systems: critical evaluation

Julia Sohr, Wolfgang Voigt

Institute of Inorganic Chemistry, TU Bergakademie Freiberg, 09596 Freiberg, Germany

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Abstract

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 consists of 7 data sets in the pure binary system lithium sulfate - water. Moreover, 36 ternary, 28 quaternary, 10 reciprocal and 6 higher systems containing lithium sulfate have been compiled.

Solubility data of the binary system are evaluated and best values recommended. The course of the solubility curve is tested against thermodynamic data.

14 of the compiled ternary systems were investigated by at least two different authors, which allows their evaluation. For the following systems at least three independent publications are available: $Li_2SO_4 + Na_2SO_4 + H_2O$ (298 K), $Li_2SO_4 + K_2SO_4 + H_2O$ (298 K), $Li_2SO_4 + MgSO_4 + H_2O$ (298), $Li_2SO_4 + CoSO_4 + H_2O$ (298 K), $Li_2SO_4 + CuSO_4 + H_2O$ (298 K), $Li_2SO_4 + Al_2(SO_4)_3 + H_2O$ (273 K) and $Li_2SO_4 + (NH_4)_2SO_4 + H_2O$ (298 K).

Focusing on the crystallization fields of all possible lithium sulfate salts one can find double salts and solid solutions mainly between lithium sulfate and alkali metal sulfates. For all other sulfates only calcium sulfate forms a double salt with lithium sulfate ($Li_2SO_4 \cdot CaSO_4 \cdot 3H_2O$ at 323 K).

The addition of any salt MSO_4 (M – bivalent metal ion) to a lithium sulfate solution decreases the solubility of lithium sulfate monohydrate in the same way. This allows a general evaluation of lithium sulfate solubility in the presence of bivalent metal sulfates and thus a estimation of single authors' data.

E-mail address: julia.sohr@chemie.tu-freiberg.de; wolfgang.voigt@chemie.tu-freiberg.de

Condensation-type complex formation reaction of Al(III) with D-gluconate in hyperalkaline NaOH/NaAl(OH)$_4$ solutions

Ágost Gyula Tasi,[1,2] Attila Pallagi,[1,2] Gábor Peintler,[2,3] István Pálinkó,[2,4] Pál Sipos[1,2]

[1]Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720, Hungary
[2]Materials and Solution Structure Research Group, University of Szeged (Hungary)
[3]Department of Physical Chemistry and Material Science, University of Szeged, Aradi Vértanúk tere 1, Szeged, H-6720, Hungary
[4]Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720, Hungary

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Abstract

According to several authors, there is no interaction between the D-gluconate ($Gluc^-$) and the Al(III) species present in strongly alkaline solutions [1,2]. In this study, first the interaction between $Al(OH)_4^-$ and $Gluc^-$ under hyperalkaline conditions was proven *via* multinuclear NMR, Raman spectroscopic and freezing-point depression measurements. The ^{27}Al NMR peak of the $Al(OH)_4^-$ species gradually melted into the baseline with increasing concentration of $Gluc^-$ ($[Gluc^-]_{tot}$). In the Raman spectra, the intensity of the symmetric stretching (ν_1–AlO_4) of $Al(OH)_4^-(aq)$ also decreased. The freezing-point depression also proved the complexation reaction, as decrease of the number of the species in the alkaline solutions was observed.

Potentiometric titrations (with H_2/Pt electrode) were also performed, but these measurements, in agreement with the published data, did not indicate complexation in solutions with pH ≥ 12. This suggests that the complexation reaction was a pH-independent process, i.e. a condensation reaction should take place.

To determine the apparent stability constant of the complex, ^{1}H NMR spectra were measured of solution series with $[OH^-]_{tot} = 0.500$; 1.000; 1.667 M and at constant $[Gluc^-]_{tot}$, while $[Al(OH)_4^-]_{tot}$ were increased within the series. Fitting of the integrated peaks associated with the complexed ligand resulted in a formation of $\log K_{1,1} = 2.4 \pm 0.4$ with an Al(III) : $Gluc^-$ ratio of 1:1. This averaged value was also confirmed *via* polarimetric measurements of solutions with $[OH^-]_{tot} = 0.250$ and 0.650 M. These results, together with further conductometric titrations supported our previous hypothesis, proving the pH-independence of the complex formation with the following probable reaction equation:

$$Al(OH)_4^- + Gluc^- \rightleftharpoons \left[Al(OH)_2(Gluc)\right]^{2-} + 2H_2O$$

The temperature-dependence of ^{1}H NMR spectra showed that the alcoholate groups on the 2nd and 3rd C-atoms were most likely to be bound to the $Al(OH)_4^-$. Upon these observations, the assumed geometry of the pseudo-tetrahedral "AlGluc" complex, forming in strongly alkaline solutions was optimized at Hartree-Fock level of theory, applying the 6-31G** basis set.

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E-mail address: sipos@chem.u-szeged.hu

Properties of solvent-shared and contact ion pairs in aqueous Ln(III) and An(III) perchlorate solutions

M. Trumm, P. Lindqvist-Reis, B. Schimmelpfennig

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

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Abstract

Several researchers have previously reported that the luminescence lifetime of Eu(III) in aqueous solution decreases substantially with increasing concentration of perchlorate ions [1-4]. The reason for this luminescence quenching for Eu(III) was not understood up to now and has been a matter of controversy [1-4]. In contrast to water molecules or hydroxide ions, both of which quench the luminescence lifetime of Eu(III) and Cm(III) through multi-phonon coupling with certain OH vibrational overtones, the corresponding mechanism for perchlorate is unfavorable and does not result in quenching. It has even been proposed that the reduced Eu(III) lifetime is a consequence of an increased hydration number [1-3]. Considering that the hydration numbers of Eu(III) and Cm(III) may change between eight and nine depending on the chemical environment and temperature [5], an increase of the hydration number from nine to almost twelve for Eu(III), corresponding to a reduction of the lifetime from 110 to 87 µs [3], is not realistic. Therefore, other mechanisms should account for the quenching. In the present work, we present time-resolved laser-induced fluorescence spectroscopy (TRLFS) and vibronic sideband spectroscopy studies of Eu(III), Gd(III), and Cm(III) in aqueous solutions at different concentrations of background electrolytes of $HClO_4$, $NaClO_4$ and $La(ClO_4)_3$. The results clearly confirm that perchlorate ions residing in the second hydration spheres of the hydrated metal ions form weak hydrogen bonds with the water molecules of the first hydration sphere. This affects the OH-vibrational manifolds of the water molecules in the first hydration sphere, which is expressed as a shift of the OH stretching vibrations to higher frequencies. These blue-shifts correlate with the reduced lifetimes of Eu(III) and Cm(III).

In order to obtain structural information, molecular dynamics (MD) simulations on a dilute $Cm(ClO_4)_3$ aqueous solution were performed. The results show two favorable solvent-shared ion pairs with either two or three perchlorate ions located in the second hydration sphere of the curium ion (Fig. 1). The formation of solvent-shared ion pairs have small effects on the coordination geometry of the $[Cm(H_2O)_9]^{3+}$ ion, which feature a tricapped trigonal prismatic coordination geometry. However, these solvent-shared ion pairs substantially weaken the hydrogen bonds between the perchlorate ions and the water molecules in the first hydration sphere, increasing the OH bond strength of those water molecules. This, in turn, generates a significant blue-shift of the OH stretching vibrations. Vibrational modes calculated with DFT, RICC2 and ab initio MD techniques concur with experimental findings. For both structures depicted in Fig. 1, the theoretically predicted blue-shift lies between 100-210 cm^{-1}. This is slightly smaller than the shifts of about 270 cm^{-1} as found for Cm(III) and Gd(III) in perchloric acid using vibronic sideband spectroscopy (Fig. 2).

The possible formation of inner-sphere complexes of Cm(III) with perchlorate, which may occur only at extreme perchlorate ion concentrations, is investigated with TRLFS as well as theoretically using thermodynamic cycles.

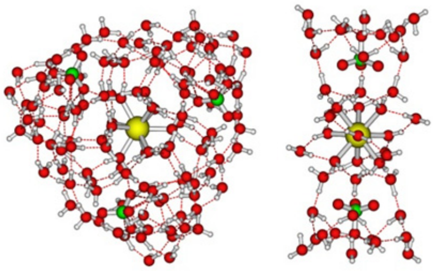

Figure 1 *Optimized structures of the two most occuring geometries in the MD simulation.*

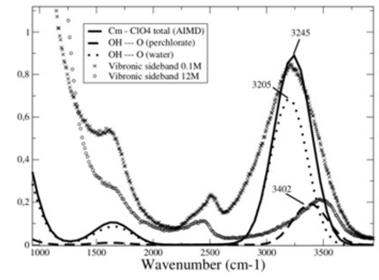

Figure 2 *Simulated AIMD/DFT power spectrum of $Cm(ClO_4)_3(H_2O)_{216}$ compared to the vibronic sideband spectrum at 0.1M and 12M $HClO_4$.*

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E-mail address: michael.trumm@kit.edu

Study of Np(V) complexation with propionate and lactate at varying ionic strengths and temperatures

A. N. Vasiliev,[1,2] N. L. Banik,[1] R. Marsac,[1] C. M. Marquardt,[1] S. N. Kalmykov[2]

[1]*Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany*
[2]*Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russia*

Abstract

Np-237 (Np) (half-life $2.14\cdot10^6$ y) is one of the relevant elements in nuclear waste disposal. Neptunium will be in the pentavalent oxidation state in many non-reducing chemical environments. Natural clay formations are considered as potential host rocks for deep geological repositories of nuclear waste, because of their low permeability and high retention properties for radionuclides via sorption processes. Small organic molecules, however, such as lactate and propionate exist in clay rock pore water and might enhance Np mobility because of the formation of soluble complexes. Because of the radioactive decay heat, temperatures in the near-field of a nuclear waste repository will significantly increase after closure and might impact radionuclide retention processes in certain scenarios. Therefore, the complexation of Np by lactate and propionate at elevated temperatures at varying ionic strengths is investigated in the present work.

Two methods were applied and compared for the determination of NpO_2^+ complexation with propionate ([Prop] = 0-0.30 mol/L) and lactate ([Lact] = 0-0.33 mol/L), namely UV-Vis/NIR spectroscopy and liquid-liquid extraction (LLE) technique with isoamyl alcohol solution containing 10^{-3} M TTA and $5\cdot10^{-4}$ M 1,10-phenanthroline [1]. Measurements were performed at 0.5-2.5 M NaCl solutions and different temperatures (20-85 °C). The maximum of the absorption band of the neptunyl aqua ion (NpO_2^+) at 980 nm shifts with increasing ligand concentration to 983 nm (NpO_2Prop) and 986 nm (NpO_2Lact) while its absorption intensity decreases. In the extraction experiment, the distribution ratio of [Np-org]/[Np-aq] decreases with increasing ligand concentration. Both methods were shown to give very consistent conditional stability constants for given conditions. Slope analysis of the results indicates a 1:1 Np(V) complex formation for propionate and lactate. The SIT approach was used to calculate equilibrium constants $\beta^0(T)$ at zero ionic strength from the experimental data. Log $\beta^0(T)$ is found linearly correlated to 1/T, evidencing that heat capacity equals 0. Molal reaction enthalpy and entropy ($\Delta_rH^0_m$ and $\Delta_rS^0_m$) could therefore be derived from the integrated van't Hoff equation. We found, for propionate, log $\beta^0(298.15K) = 1.24 \pm 0.04$, $\Delta\varepsilon$ (i.e. SIT parameter) $= -0.17\pm 0.03$, $\Delta_rH^0_m = 16.7 \pm 2.7$ kJ·M^{-1} and $\Delta_rS^0_m = 80 \pm 1$ J·M^{-1}·K^{-1}. For lactate, we found log $\beta^0(298.15K) = 2.0 \pm 0.1$, $\Delta\varepsilon$ (i.e. SIT parameter) $= -0.15\pm 0.09$, $\Delta_rH^0_m = -3.4 \pm 1.4$ kJ·M^{-1} and $\Delta_rS^0_m = 23.2\pm 4.5$ J·M^{-1}·K^{-1}. Data for log $\beta^0(298.15K)$ are in agreement with literature values for acetate and lactate [2].

The present study shows that Np complexation to both propionate and lactate is significantly impacted by temperature and salinity.

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E-mail address: stavrogin.aleksandr@yandex.ru

Interaction of Eu(III) and Cm(III) with $Mg(OH)_2(cr)$ in the system Mg^{2+}-Na^+-Cl^--OH^--H_2O

M. Wiedemann, V. Metz, T. Rabung, N. Finck, H. Geckeis

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

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Abstract

A reliable description of the behavior of actinides in the near-field is necessary in long-term safety analyses for radioactive waste repositories in deep geological formations. Under reducing conditions, which develop after closure of a deep underground repository, actinides are expected to prevail in tri- and tetravalent redox states, e.g. Pu(III/IV), Am(III), Cm(III). For the Asse II salt mine (Germany) and the Waste Isolation Pilot Plant (USA), where low / intermediate level radioactive waste products are emplaced, $Mg(OH)_2(cr)$-bearing materials and MgO are used as sealing materials and engineered buffer, respectively [1,2]. Recent studies on co-precipitation of Eu(III) [3] as well as Cm(III) [4] with $Mg(OH)_2(cr)$ in $MgCl_2$ systems at low ionic strength ($I = 0.2$ molal) show an incorporation of the lanthanides and actinides into the octahedral $Mg(OH)_2$ structure. Yet, there is no published study available dealing with the interaction of actinides / lanthanides with $Mg(OH)_2(cr)$ impacting solubility and retention processes at elevated ionic strength.

The present study focuses on recrystallization and co-precipitation experiments, where the structure of Eu(III)-bearing $Mg(OH)_2(cr)$ and the speciation of Eu(III) and Cm(III) sorption species are analyzed by means of extended X-ray absorption fine structure (EXAFS) and time-resolved laser fluorescence spectroscopy (TRLFS). Recrystallization experiments were prepared with $MgCl_2 \pm NaCl \pm NaClO_4$ solutions as background electrolytes ($0.15 \leq I \leq 5.2$ molal), adjusted in a disposal relevant range of $8.7 \leq pH_m \leq 9.0$ and doped with $[Cm] = 1\cdot10^{-7}$ molal. Synthetic $Mg(OH)_2$:Eu(cr) was prepared by co-precipitation of 0.4 molal $MgCl_2$ solution (+ 4 molal NaCl solution) with 2.1 molal NH_4OH solution and 700 ppm of Eu(III). TRLFS kinetic studies of the Cm (III) sorption mechanism on $Mg(OH)_2(cr)$ indicate the formation of sorption / incorporation species. At lower ionic strengths ($I \leq 1.2$ molal) the subsequent formed fluorescence peaks are strongly red-shifted which hints to an incorporated species. EXAFS investigations of the co-precipitation experiments indicate an incorporation of Eu(III) into a distorted octahedral $Mg(OH)_2$ structure. No significant effect of the ionic strength on the incorporation mechanism is observed for the co-precipitation experiments. Lifetimes from Eu(III)-TRLFS studies of co-precipitated $Mg(OH)_2(cr)$ indicate the presence of at least two species with 126 ± 12 µs (8.0 ± 0.8 H_2O) and 296 ± 12 µs (3.0 ± 0.1 H_2O). The results of the present Eu(III)-TRLFS studies are in agreement with conclusions drawn from previous Cm(III)-TRLFS studies of $Mg(OH)_2(cr)$ recrystallization experiments [5].

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E-mail address: martin.wiedemann@kit.edu

Experimental determination of lead solubility in the carbonate systems to high ionic strengths: A Pitzer model description[A]

Yongliang Xiong

Repository Performance Dept. 6212, Sandia National Laboratories[B], 4100 National Parks Highway, Carlsbad, NM 8822, USA

Abstract

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy (DOE) repository in southeast New Mexico for defense-related transuranic (TRU) waste. The repository, which opened in March 1999, is located at a subsurface depth of 655 m in the Salado Fm., a Permian bedded-salt formation. It is planned to use a significant amount of lead as a radiation-shielding material for wastes with significant γ-radiation placed in the WIPP. Carbonate is an important inorganic ligand in the WIPP brines such as Generic Weep Brine (GWB), from the Salado Fm. at the stratigraphic horizon of the repository, and Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) from the underlying Castile Fm. These two brines are important to the Performance Assessment (PA) of the repository. When lead is corroded under anoxic conditions in carbonate-containing brines, lead carbonate, cerussite ($PbCO_3(cr)$), is expected to form. Therefore, the accurate knowledge of solubilities of cerussite in a wide range of ionic strengths has important bearings on the chemical behavior in the repository.

A long-term study on the solubilities of cerussite in $NaHCO_3$ + NaCl, Na_2CO_3 + NaCl and $NaHCO_3$ + Na_2CO_3 solutions at room temperature and at high ionic strengths up to 6.15 $mol \cdot kg^{-1}$ has been conducted at Sandia National Laboratories (SNL) Carlsbad Facility. In this presentation, in conjunction with the thermodynamic parameters from the literature [1-4], a Pitzer model is developed for the accurate descriptions of the the Na^+—Pb^{2+}—Cl^-—$HCO3^-$—CO_3^{2-} system. The platform for the model development is the computer program EQ3/6 Version 8.0a [5-6].

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E-mail address: yxiong@sandia.gov

The liquid-solid phase equilibrium of the system $Na^+//Cl^-$, SO_4^{2-}, NO_3^--H_2O at 278, 273, 268, 258 K

Xia Zhang,[1] Xueli Huang[1,2]

[1] *College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang, 830046, China*
[2] *Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education & Xinjiang Uygur Autonomous Region, Xinjiang University, Urumqi, 830046, China*

Abstract

In Tu Lu Fan region of Xinjiang province of China, nitrate deposits are found in an area about 15000 km^2, the proven reserve of which reaches 1.8×10^7 ton. The deposits are divided into two main kinds: brine and solid ore. In the majority of the solid ore, there exist the salts such as NaCl, Na_2SO_4, $NaNO_3$ and $NaNO_3\cdot Na_2SO_4\cdot H_2O$, etc.. By leaching this ore with water, the brine containing Na^+, Cl^-, SO_4^{2-}, NO_3^-, H_2O can be obtained, and used to manufacture sodium nitrate or potassium nitrate by reacting with KCl [1,2]. It is well known that study on liquid-solid phase equilibrium be very important for exploiting salt-lake brine resources. For the system $Na^+//Cl^-$, SO_4^{2-}, NO_3^-–H_2O, solubilities in liquid-solid equilibrium at 298 K can be found in some compilations [3,4]. However, solubilities in liquid-solid equilibrium at lower temperature haven't been reported so far.

In this work, The equilibrium solubilities of this system were determined by isothermal dissolution method at 278, 273, 268, 258 K. According to the experimental data, the liquid-solid equilibrium phase diagram were plotted. As shown in Fig. 1 (the unit: mol/mol(SO_4^{2-}+2NO_3^-+2Cl^-)), there are one invariant points with three salts ($NaNO_3$+$Na_2SO_4\cdot 10H_2O$ +NaCl or $NaCl\cdot 2H_2O$), three univariant curves with two salts, three regions of crystallization with single salt. The double-salt $Na_2SO_4\cdot NaNO_3\cdot H_2O$ does not exist when temperature is below 278 K. The area of crystallization of $Na_2SO_4\cdot 10H_2O$ is far larger than those of $NaNO_3$ and NaCl or $NaCl\cdot 2H_2O$, that is, the content of SO_4^{2-} in solution at lower temperature is very small.

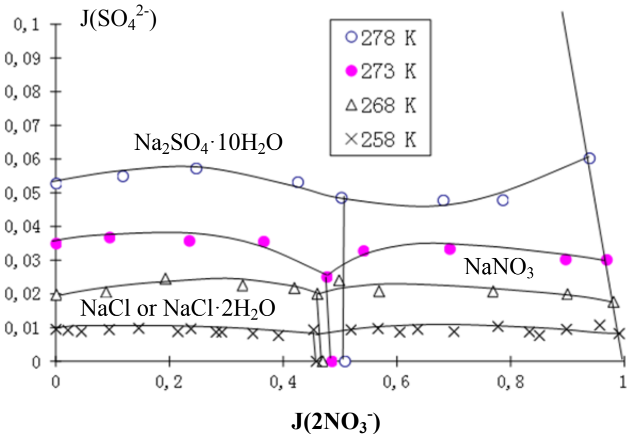

Figure 1 *The phase diagram at 278, 273, 268, 258 K*

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E-mail address: xuelih@163.com

Thermodynamic description of Tc(IV) solubility and hydrolysis in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions

E. Yalcintas, X. Gaona, M. Altmaier, H. Geckeis

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

Abstract

Technetium–99 is a β–emitting fission product highly relevant for the safety assessment of waste repositories for radioactive materials due to its significant inventory in spent nuclear fuel, long half-life ($t_{½}$ ~211.000 a) and redox sensitivity. Under sub-oxic/oxidizing conditions, Tc(VII) is the most stable oxidation state of Tc and exists as 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 in 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 the performance assessment of repositories for radioactive waste disposal.

In the present study, the solubility of Tc(IV) was investigated from undersaturation conditions in 0.5–5.0 M NaCl, 0.25–4.5 M $MgCl_2$ and 0.25–4.5 M $CaCl_2$ solutions in the pH_c range 2–14.6. Experiments were performed at 22 ± 2°C in Ar gloveboxes with < 2 ppm O_2. Strongly reducing conditions (pH + pe < 4) were chemically set for each independent solubility sample with $Na_2S_2O_4$, $SnCl_2$ or Fe powder. Technetium concentration, pH_c and E_h values were monitored at regular time intervals. Thermodynamic equilibrium was assumed after repeated measurements with constant [Tc] and pH_c. 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 also characterized by XRD, SEM–EDS and quantitative chemical analysis.

Solvent extraction and XANES analysis confirm the predominance of Tc(IV) in all the systems evaluated. Experimental solubility data determined in dilute NaCl and $MgCl_2$ solutions agree well with thermodynamic calculations considering the Tc(IV) chemical model and data selected by the NEA–TDB [1]. In the acidic pH range, a very significant increase in the solubility (up to 4 orders of magnitude) is observed with increasing ionic strength for all investigated salt systems. In concentrated alkaline NaCl solutions, the same speciation as for diluted systems is retained (e.g. predominance of $TcO(OH)_3^-$), 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 $Mg_x[TcO(OH)_y]^{2x-2-y}$ and $Ca_x[TcO(OH)_y]^{2x-2-y}$ ternary species is proposed based on the slope analysis of the corresponding solubility curves and analogy with actinide chemistry. XRD, SEM–EDS and chemical analysis confirm that $TcO_2{\cdot}1.6H_2O(s)$ is the solid phase controlling the solubility of Tc(IV) in all the saline systems evaluated. Chemical, thermodynamic and activity models (SIT, Pitzer) are derived for the system Tc^{4+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–H_2O based upon the newly generated experimental solubility data.

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E-mail address: ezgi.yalcintas@kit.edu

List of participants

Altmaier, Marcus	Karlsruhe Institute of Technology *Germany*	marcus.altmaier@kit.edu
Atanassova, Maria	CNRS *France*	mickael.puerto@iphc.cnrs.fr
Balarew, Christo	Bulgarian Academy of Sciences *Bulgaria*	balarew@svr.igic.bas.bg
Baluja, Shipra	Saurashtra University *India*	shipra_baluja@rediffmail.com
Baumann, Alexander	Karlsruhe Institute of Technology *Germany*	alexander.baumann@kit.edu
Bazarkina, Elena	CNRS *France*	elena.bazarkina@univ-lorraine.fr
Behnejad, Hassan	University College of Science *Iran*	Behnejad@khayam.ut.ac.ir
Bellefleur, Alexandre	EDF *France*	alexandre.bellefleur@edf.fr
Benazzouz, Adrien	University of Lille *France*	adrienbenazzouz@aol.com
Bendová, Magdalena	Institute of Chemical Process Fundamentals Prague *Czech Republic*	Bendova@icpf.cas.cz
Bénézeth, Pascale	CNRS *France*	Pascale.benezeth@get.obs-mip.fr
Bette, Sebastian	TU Bergakademie Freiberg *Germany*	sebastian.bette@chemie.tu-freiberg.de
Bogachev, Nikita	Saint-Petersburg State University *Russia*	allanfrack@yandex.ru
Bok, Frank	Helmholz-Zentrum Dresden-Rossendorf *Germany*	f.bok@hzdr.de
Brandt, Felix	Forschungszentrum Jülich *Germany*	f.brandt@fz-juelich.de
Chebil, Latifa	University Of Lorraine *France*	latifa.chebil@univ-lorraine.fr
Cho, Hye-Ryun	Korea Atomic Energy Research Institute *South Korea*	hrcho@kaeri.re.kr
Davidian, Anna	Saint-Petersburg State University *Russia*	AGDavidian@yandex.ru

De Visscher, Alex	University of Calgary *Canada*	adevissc@ucalgary.ca
Deng, Tianlong	Tianjin University of Science and Technology *China*	tldeng@tust.edu.cn
Denoncourt-Pottinger, Julie	accompanying person of Alex de Visscher *Canada*	adevissc@ucalgary.ca
Duro, Lara	Amphos 21 Consulting S.L. *Spain*	lara.duro@amphos21.com
Fanghänel, Susanne	Karlsruhe Institute of Technology *Germany*	susanne.fanghaenel@kit.edu
Fanghänel, Thomas	JRC-Institute for Transuranium Elements *European Commission*	thomas.fanghaenel@ec.europa.eu
Filella, Montserrat	University of Geneva *Switzerland*	Montserrat.Filella@unige.ch
Freyer, Daniela	TU Bergakademie Freiberg *Germany*	daniela.freyer@chemie.tu-freiberg.de
Furia, Emilia	University of Calabria *Italy*	e.furia@unical.it
Gadzuric, Slobodan	University Novi Sad *Serbia*	slobodan.gadzuric@dh.uns.ac.rs
Gamsjäger, Heinz	Montanuniversität *Austria*	gamsjaeg@unileoben.ac.at
Gamsjäger, Heidrun	accompayning person of Heinz Gamsjäger *Austria*	gamsjaeg@unileoben.ac.at
Gaona, Xavier	Karlsruhe Institue of Technology *Germany*	xavier.gaona@kit.edu
Gilani, H.Ghanadzadeh	University of Guilan *Iran*	hggilani@guilan.ac.ir
González-Siso, Maria R.	Amphos 21Consulting S.L. *Spain*	maria.rosa.siso@amphos21.com
Gorbunov, Artem O.	Saint-Petersburg State University *Russia*	artyom-laptop@yandex.ru
Graff, Anaïs	EDF *France*	anais.graff@edf.fr
Grenthe, Ingmar	KTH - Royal Institute of Technology *Sweden*	ingmarg@kth.se

Gumiński, Cezary	University of Warsaw *Poland*	cegie@chem.uw.edu.pl
Gusev, Ilya	Saint-Petersburg State University *Russia*	gusev.ilya.0304@gmail.com
Haghtalab, Ali	Tarbiat Modares University *Iran*	haghtala@modares.ac.ir
Hefter, Glenn	Murdoch University *Australia*	g.hefter@murdoch.edu.au
Hefter, Maria	accompanying person of Glenn Hefter *Australia*	g.hefter@murdoch.edu.au
Herm, Michel	Karlsruhe Institute of Technology *Germany*	michel.herm@kit.edu
Hinz, Katja	Karlsruhe Institute of Technology *Germany*	katja.hinz@kit.edu
Huang, Xueli	Xinjiang University *China*	xuelih@163.com
Hummel, Wolfgang	Paul Scherrer Institut *Switzerland*	wolfgang.hummel@psi.ch
Hussein, Rasha	TU Bergakademie Freiberg *Germany*	rascha_de@yahoo.com
Kaden, Peter	Karlsruhe Institute of Technology *Germany*	peter.kaden@kit.edu
Kamburov, Stoyan	Bulgarian Academy of Sciences *Bulgaria*	s.kamburov@svr.igic.bas.bg
Klamt, Andreas	COSMOlogic GmbH&CoKG *Germany*	klamt@cosmologic.de
Klinkenberg, Martina	Forschungszentrum Jülich *Germany*	m.klinkenberg@fz-juelich.de
Kobayashi, Taishi	Kyoto University *Japan*	kobayashi@nucleng.kyoto-u.ac.jp
Königsberger, Erich	Murdoch University *Australia*	E.Koenigsberger@murdoch.edu.au
Königsberger, Lan-Chi	Murdoch University *Australia*	L.Koenigsberger@murdoch.edu.au
Kulik, Dmitrii	Paul Scherrer Institut *Switzerland*	dmitrii.kulik@psi.ch
Kundal, Haresh	accompanying person *India*	hlkundal@gmail.com

Lameche, Charaf E.	Ferhat Abbas University *Algeria*	charaf.e-lameche@hotmail.com
Lélias, Anne	CEA *France*	anne.lelias@cea.fr
Lempinen, Janne	University of Helsinki *Finland*	janne.lempinen@helsinki.fi
Lindqvist-Reis, Patric	Karlsruhe Institute of Technology *Germany*	patric.lindqvist@kit.edu
Lukowicz, Thomas	ENSCL *France*	lukowicz.thomas@googlemail.com
Lützenkirchen, Johannes	Karlsruhe Institute of Technology *Germany*	johannes.luetzenkirchen@kit.edu
Magalhães, Clara	University of Aveiro *Portugal*	mclara@ua.pt
Makaev, Sergey	Russian Academy of Sciences *Russia*	makaev@gmail.com
Marcus, Yizhak	Hebrew University of Jerusalem *Israel*	ymarcus@vms.huji.ac.il
Marcus, Tova	accompanying person of Yizhak Marcus *Israel*	ymarcus@vms.huji.ac.il
Marquardt, Christian	Karlsruhe Institute of Technology *Germany*	christian.marquardt@kit.edu
Matsuda, Hiroyuki	Nihon University *Japan*	matsuda.hiroyuki@nihon-u.ac.jp
Mesones, Javier	Universitat Rovira I Virgili *Spain*	alberto.coronas@urv.cat
Metz, Volker	Karlsruhe Institute of Technology *Germany*	volker.metz@kit.edu
Miron, G. Dan	ETH Zurich *Switzerland*	dan.miron@erdw.ethz.ch
Mühlbauer, Andrea	University of Lille *France*	andrea.muehlbauer@ed.univ-lille1.fr
Orucoglu, Esra	Istanbul Technical University *Turkey*	orucoglu@itu.edu.tr
Panak, Petra	University of Heidelberg *Germany*	petra.panak@kit.edu
Pestova, Olga	Saint-Petersburg State University *Russia*	pestova-1980@mail.ru

Petrov, Vladimir	Lomonosov Moscow State University *Russia*	vladimir.g.petrov@gmail.com
Plakhova, Tatiana	Lomonosov Moscow State University *Russia*	tatiana.v.plakhova@gmail.com
Polly, Robert	Karlsruhe Institute of Technology *Germany*	robert.polly@kit.edu
Qiu, Liyan	Atomic Energy of Canada Limited *Canada*	qiul@aecl.ca
Ragoussi, Maria-Eleni	OECD – Nuclear Energy Agency *France*	maria-eleni.ragoussi@oecd.org
Rajabu, Hamidu	Ferhat Abbas University *Algeria*	hammy.duh@gmail.com
Reed, Donald T.	Los Alamos National Laboratory *USA*	dreed@lanl.gov
Rodrigues, David	Institut de Physique Nucléaire d'Orsay *France*	rodrigues@ipno.in2p3.fr
Romanchuk, Anna	Lomonosov Moscow State University *Russia*	romanchuk.anna@gmail.com
Rowland, Darren	Murdoch University *Australia*	d.rowland@murdoch.edu.au
Runde, Wolfgang	Los Alamos National Laboratory *USA*	runde@lanl.gov
Salminen, Justin	VTT Technical Research Center of Finland *Finland*	Justin.salminen@vtt.fi
Samarov, Artemiy	Saint-Petersburg State University *Russia*	samarov@yandex.ru
Sangster, James	Sangster Research Laboratories *Canada*	James.Sangster@polymtl.ca
Schäfer, Thorsten	Karlsruhe Institute of Technology *Germany*	thorsten.schaefer@kit.edu
Schepperle, Julian	Karlsruhe Institute of Technology *Germany*	julian.schepperle@kit.edu
Schmidt, Horst	TU Bergakademie Freiberg *Germany*	horst.schmidt@chemie.tu-freiberg.de
Semenov, Konstantin N.	Saint-Petersburg State University *Russia*	semenov1986@yandex.ru

Shojaeian, Abolfazl	Tarbiat Modares University *Iran*	a_shojaeian@yahoo.com, a.shojaeian@modares.ac.ir
Simonnet, Marie	Institut de Physique Nucléaire d'Orsay *France*	simonnet@ipno.in2p3.fr
Sipos, Pál	University of Szeged *Hungary*	sipos@chem.u-szeged.hu
Skerencak-Frech, Andrej	Karlsruhe Institute of Technology *Germany*	andrej.skerencak@kit.edu
Skripkin, Mikhail	Saint-Petersburg State University *Russia*	skripkin1965@yandex.ru
Sohr, Julia	TU Bergakademie Freiberg *Germany*	Julia.Sohr@chemie.tu-freiberg.de
Spahiu, Kastriot	SKB *Sweden*	kastriot.spahiu@skb.se
Tasi, Ágost G.	University of Szeged *Hungary*	Tasi.Agost.Gyula@stud.u-szeged.hu
Tepavitcharova, Stefka	Bulgarian Academy of Sciences *Bulgaria*	stepav@svr.igic.bas.bg
Thomsen, Kaj	Technical University of Denmark *Denmark*	KTH@kt.dtu.dk
Tikhonov, Nikolay A.	Lomonosov Moscow State University *Russia*	niktandr@yandex.ru
Toikka, Alexander	Saint-Petersburg State University *Russia*	alexander.toikka@chem.spbu.ru
Truche, Laurent	CNRS *France*	Laurent.truche@univ-lorraine.fr
Trumm, Michael	Karlsruhe Institute of Technology *Germany*	michael.trumm@kit.edu
Valyashko, Vladimir	Russian Academy of Sciences *Russia*	valyashko@mail.ru
Vasiliev, Aleksandr N.	Karlsruhe Institute of Technology *Germany*	aleksandr.vasiliev@partner.kit.edu
Voigt, Wolfgang	TU Bergakademie Freiberg *Germany*	Wolfgang.Voigt@chemie.tu-freiberg.de
Waghorne, Earle	University College Dublin *Ireland*	earle.waghorne@ucd.ie
Wang, Peiming	OLI Systems, Inc. *USA*	PWANG@OLISYSTEMS.COM

Wiedemann, Martin	Karlsruhe Institute of Technology *Germany*	martin.wiedemann@kit.edu
Wong, Man Shan	accompanying person of Wolfgang Hummel *Switzerland*	wolfgang.hummel@psi.ch
Xiong, Yongliang	Sandia National Laboratories *USA*	yxiong@sandia.gov
Yalcintas, Ezgi	Karlsruhe Institute of Technology *Germany*	ezgi.yalcintas@kit.edu
Zeng, Dewen	Central South University, Lu Shan Nan Lu *China*	dewen_zeng@hotmail.com

	Monday	Tuesday	Wednesday	Thursday	Friday	
08:30	Opening + H. Gamsj.	I. Grenthe	M. Bendova	W. Runde	S. Gadzuric	08:30
09:15	H. Gamsjäger	O 12 M.-E. Ragoussi	O 18 E. Waghorne	O 24 C. Guminski	O 35 S. Bette	09:15
09:40	O 01 E. Königsberger	O 13 Y. Marcus	O 19 A. Toikka	O 25 Y. Xiong	O 36 A. Skerencak	09:40
10:05	coffee	coffee	coffee	coffee	coffee	10:05
10:35	O 02 P. Sipos	O 14 D.A. Kulik	O 20 Th. Lukowicz	O 26 M. Skripkin	O 37 N.A. Tikhonov	10:35
11:00	O 03 X. Gaona	O 15 D. Rowland	O 21 L. Chebil	O 27 A. Lélias	O 38 G. Hefter	11:00
11:25	O 04 P. Wang	O 16 G.D. Miron	O 22 E. Furia	O 28 D. Reed,	O 39 D. Rodrigues	11:25
11:50	O 05 F. Brandt	O 17 A. Klamt	O 23 H. Matsuda	O 29 L. Truche	O 40 J. Lempinen	11:50
12:15	Lunch	Lunch	Lunch	Lunch	Closing	12:15
14:00	M. Filella	14:00 V. Metz	Conf.Tour	W. Voigt		14:00
14:45	O 06 E.F. Bazarkina	14:30 K. Spahiu		O 30 S. Makaev		14:45
15:10	O 07 J. Salminen	15:00 W. Hummel		O 31 T. Deng		15:10
15:35	coffee	coffee		coffee		15:35
16:05	O 08 C.M. Magalhães	16:00 P. Panak		O 32 D. Zeng		16:05
16:30	O 09 K. Thomsen	16:30 L. Duro		O 33 O.N. Pestova		16:30
16:55	O 10 J. Mesones	17:00 Th. Fanghänel		O 34 Chr. Balarew		16:55
17:20	O 11 A. Benazzouz					17:20
17:45						17:45
18:00		Poster session	Conf.Tour			18:00
19:00				Conf. Dinner		19:00