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Abstracts

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INVITED SPEAKERS

THE DISPERSION OF ANTIMONY IN SOLUTION FROM OXIDIZING ORE DEPOSITS

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A series of comprehensive reviews by Filella *et al.* [1-3] has illuminated our understanding of the behaviour of Sb in the natural environment. However, the geochemistry of Sb above the water table (supergene zone) in the vicinity of oxidizing primary ores is still poorly understood. Several hundred primary Sb minerals (sulfides and sulfosalts) are known and all are essentially insoluble in water under ambient conditions. In the supergene zone these are reacted to give secondary phases, which act as metal ion buffers, and control in conjunction with other processes the dispersion of Sb in surface and soil waters. Some 40 such minerals are known [4]; many are very rare, but others are commonly found and these have become the focus of study in an effort to elucidate the geochemical behaviour of the element in such settings. Both Sb(III) and Sb(V) are present in the supergene zone, with Sb(V) being the most stable oxidation state. Previous approaches to understanding Sb geochemistry have been hampered by the lack of reliable thermochemical data for cervantite, Sb_2O_4 , and the fact that $\text{Sb}_2\text{O}_5(\text{s})$ has been used as a proxy for the secondary Sb(V) minerals [5]. This compound does not exist in Nature and other phases must be accounted for. The erroneous conclusion that Sb(V) is quite mobile in the supergene environment has been promulgated in the literature as a result.

Of the secondary Sb(V) minerals, salts of $\text{Sb}(\text{OH})_6^-$ such as mopungite, $\text{NaSb}(\text{OH})_6$, bottinoite, $\text{Ni}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$, and brandholzite, $\text{Mg}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$, are important in some oxidized zones, but members of the pyrochlore group are particularly significant. They include bindheimite, $\text{Pb}_{1-2}\text{Sb}_2(\text{O},\text{OH})_7$, roméite, $\text{Ca}_{1-2}\text{Sb}_2(\text{O},\text{OH})_7$, stetefeldtite, $\text{Ag}_{1-2}\text{Sb}_2(\text{O},\text{OH})_7$, bismutostibiconite, $\text{BiSb}_2\text{O}_6(\text{OH})$, and the enigmatic, probably non-existent phase partzite, $\text{Cu}_{1-2}\text{Sb}_2(\text{O},\text{OH})_7$.

Stibiconite, $\text{SbSb}_2\text{O}_6(\text{OH})$, is an important mixed-valence member. Aside from these, tripuhyite, FeSbO_4 , is known from at least 40 deposits and is probably more common than currently thought.

Reliable solubility data are available only for mopungite; at 25°C, its solubility is $3.18 \pm 0.2 \times 10^{-3} \text{ mol dm}^{-3}$ [6]. It has been found that bottinoite and brandholzite can be synthesised in gram quantities by aging initially amorphous precipitates formed using the double decomposition method. The Mg(II) and Ni(II) salts are orders of magnitude less soluble than mopungite at 25°C. A previous report [7] concerning the solubility products of the salts $\text{Ca}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$ is in error. Further experiments have shown that these salts cannot be prepared by double decomposition of aqueous solutions of $\text{K}[\text{Sb}(\text{OH})_6]$ and soluble Ca(II) and Pb(II) salts. Instead, X-ray amorphous precipitates form and do not crystallize at ambient temperatures during months. Warming these precipitates in contact with solution (“fast aging”) yields crystalline roméite, $\text{Ca}_{1-2}\text{Sb}_2(\text{O},\text{OH})_7$, and bindheimite, $\text{Pb}_{1-2}\text{Sb}_2(\text{O},\text{OH})_7$. Pb and Ca contents in the minerals can be controlled by stoichiometric variation of starting reagent concentrations. While they act as cation exchangers (Ca and Pb), solution concentrations of Sb(V) in equilibrium with them are very low at room temperature. In similar vein, crystalline

tripuhyite can be prepared using ammonium Fe(II) or Fe(III) sulfate. It is noteworthy that these syntheses from aqueous solution represent the first of their kind and mimic the way that the minerals are formed in Nature.

Solubility phenomena are discussed in terms of natural settings and the dispersion of Sb from them in the supergene zone. A revised Pourbaix diagram with respect to natural aqueous solutions will be presented. Implications for geochemical prospecting using Sb as a “pathfinder” element are also examined with an emphasis on deposits that carry abundant primary stibnite, Sb_2S_3 .

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Modification of Polymer Molecular Organization by Gas Sorption. Thermodynamic Aspects and Industrial Applications

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In polymer science gas-polymer interactions play a central role for the elaboration of new polymeric structures for specific applications. This is typically the case for polymer foaming¹ and for self-assembling of nano-scale structures^{2,3} where the nature of the gas and the thermodynamic conditions are essential to control. An other important applied field where gas sorption in polymers has to be documented through intensive investigations concerns the (non) controlled solubilization of light gases in the polymers serving for example in the oil industry (seals, containers, flexible hosepipes and pipe lines) for the transport of petroleum fluids. Gas concentration in the polymeric components, associated to temperature and pressure gradients, is of major concern since it may cause irreversible (explosive) damages in the on-duty materials.⁴

An experimental set-up coupling a vibrating-wire detector and a PVT-technique has been developed to simultaneously evaluate the amount of gas entering a polymer under controlled temperature and pressure and the concomitant swelling of the polymer.⁵ Scanning transitionometry has been used to determine the interaction energy during gas sorption in different polymers;⁶ the technique was also advantageously used to determine the thermophysical properties (*e.i.* isobaric thermal expansivity⁶ and glass transition⁷) of polymers submitted to gas sorption. As a matter of fact, the striking effect of gas sorption is particularly observed when the gas is in supercritical state depending on thermodynamic conditions.

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Solubility in Hydrometallurgy

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In the industrial context, the modelling of physicochemical properties of electrolyte solutions, including solubilities, is worryingly unsatisfactory. This is mainly because the models employed by industry are often purely empirical in nature, requiring that their parameters be determined by regression of data which have in general been measured on multicomponent solutions. Such models show a high degree of parameter correlation, leading to error propagation and consequent failures when attempts are made to extrapolate to smaller subsystems or beyond the ranges of parameterization. This behaviour makes meaningful process simulations virtually impossible.

Solubility is a key thermodynamic property for numerous hydrometallurgical processes, many of which contribute significantly to Australia's economy. The alumina industry, for instance, earns in excess of A\$6b export value per annum. Some of the world's largest Bayer plants are located in Australia, the world's largest alumina producer. Whilst the Bayer process is mature and often referred to as the largest recrystallisation process in the world, it still requires improved models of thermodynamic properties to increase productivity and reduce energy consumption. Such models are often based on accurate measurements of only a few properties, like heat capacities and densities. Then, the thermodynamic consistency of the model ensures that other properties, such as enthalpies and solubilities, can be predicted for conditions far exceeding current plant operating ranges. The incorporation of such models into process simulators allows better process control and permits the exploration of process modifications to increase yields and cut greenhouse gas emissions.

Our laboratory is equipped with facilities for the measurement of chemical speciation, solubilities, water activities, as well as heat capacities and densities (up to 300 °C). Results of recent measurements and new modelling approaches for systems of hydrometallurgical interest will be reviewed.

Advanced Solubility Concepts and Tools in Geochemical Modelling Related to Nuclear Waste Disposal

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If a pure solid phase of a given radionuclide (RN) is expected to reach chemical equilibrium with a specified pore fluid in underground repository then the maximum concentration (*solubility limit*) of RN can be estimated from chemical thermodynamic calculations using a well-established data base.¹ This concept has been widely used in repository safety analyses.² However, there is growing evidence that such solubility limits may over-predict by orders of magnitude the aqueous concentration $[RN]_{aq}$ of specific RNs (Ra, Am, U, Ni,...) in a repository environment. Solubility- and spectroscopic studies indicate that on a long-term scale (years to millennia) $[RN]_{aq}$ will be controlled by *solid solution* and *sorption* equilibria involving major minerals (carbonates, sulphates, clays), rather than through solubility limits fixed by pure RN phases (e.g. $RaSO_4$, $Am_2(CO_3)_3$, $USiO_4$, $NiCO_3$). Therefore, it is desirable that future safety studies use additional solubility limits based on aqueous – solid solution (Aq-SS) and/or sorption models in more realistic performance assessment calculations.³

This contribution aims at illustrating how Aq-SS models may improve our predictions on the migration properties of selected RNs, what additional process understanding of the mineral reactivity is needed, and which chemical thermodynamic tools are useful. The underlying assumption is that the *partial equilibrium* is attained between reactive minerals and pore solution in the repository environment, whereas phases with very slow dissolution/ precipitation kinetics remain metastable. The range of Aq-SS interactions is described in theory⁴ using two extreme cases: the *true equilibrium* (depicted by *solidus* and *solutus* curves on Lippmann diagram⁵) when the SS phase recrystallises rapidly; and the *minimum stoichiometric saturation* (*equal-G* curve) when the SS phase can only dissolve congruently but not recrystallise. For the true equilibrium case, the chemical speciation in all phases can be efficiently computed using a Gibbs Energy Minimization code (e.g. GEMS-PSI, <http://gems.web.psi.ch/>).

Interaction with host-rock SS minerals such as $(Ba,Sr)SO_4$, $(Ba,Sr)CO_3$ or $CaCO_3$ (calcite) may strongly influence $[RN]_{aq}$ for cations such as radium. One possible partial equilibrium scenario assumes the release of Ra into water-saturated clayey rock containing some FeS_2 , calcite and minor $(Sr,Ba)CO_3$. Upon slow recrystallisation of $(Sr,Ba)CO_3$, most radium is trapped in its crystal lattice, with a concomitant decrease in $[Ra]_{aq}$. At a second stage, FeS_2 is slowly oxidized producing sulphate ions, subsequently forming a $(Ra,Sr,Ba)SO_4$ SS, while the less stable $(Ra,Ba,Sr)CO_3$ phase is dissolved. Provided that enough sulphur is available in the system, the $[Ra]_{aq}$ is expected to decrease by orders of magnitude due to the low solubility of barium sulphate combined with the SS dilution effect for radium. Similar effects may occur in RN partitioning during the degradation of glass- and cement waste forms. Such Aq-SS systems are in the focus of current research, especially with respect to anionic RNs (I^- , IO_4^- , SeO_4^{2-} , ...), for which the incorporation into secondary SS phases may be the only effective retention mechanism.

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Solubility of M(III) and M(IV) Hydroxides/Oxides in Alkaline CaCl₂ Solutions: Formation of Ternary Ca-M-OH Complexes (M = Nd, Cm, Zr, Th, Pu)

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The solubility and aqueous speciation of actinide and other metal ions in chloride solutions is of particular interest for the storage of nuclear waste in underground salt mines. The corrosion of cementitious waste forms can lead to alkaline CaCl₂ brines. The solubilities of ZrO₂·xH₂O(s) at pH_c = 10 - 12 in 0.1 - 2.0 M CaCl₂ and of ThO₂·xH₂O(s) at pH_c = 11 - 12 in 0.5 - 4.5 M CaCl₂ increase to unexpectedly high values. The dominant aqueous species, hitherto unknown Ca-M(IV)-OH complexes, Ca₃[Zr(OH)₆]⁴⁺ and Ca₄[Th(OH)₈]⁴⁺, could be identified by analysis of the solubility data (dependence on pH_c and CaCl₂ concentration) and also by extended x-ray absorption fine structure spectroscopy (EXAFS).¹ The solubility of PuO₂·xH₂O(s) in alkaline 2.0 - 4.5 M CaCl₂ solutions also indicates the formation of Ca₄[Pu(OH)₈]⁴⁺, analogous to the behaviour of Th(IV). Trivalent lanthanides and actinides are studied by solubility experiments with Nd(OH)₃(s) in dilute to concentrated NaCl, MgCl₂ and CaCl₂ media and by time-resolved laser fluorescence spectroscopy (TRLFS) with Cm(III). In NaCl-NaOH mixtures at pH_c = 14, there is no indication for hydroxide complexes with more than three OH⁻ ligands. However, in CaCl₂ solutions above 2 molar the solubility increases already at pH_c = 11 - 12 and the evaluation of the Cm(III) emission spectra shows the formation of complexes with three, four and six OH⁻ ligands. A thermodynamic model valid for both Ca-free and Ca-containing solutions in the system M(III)-Na-Mg-Ca-Cl-H₂O (25°C) requires the formulation as ternary complexes Ca[Cm(OH)₃]²⁺, Ca₂[Cm(OH)₄]³⁺ and Ca₃[Cm(OH)₆]³⁺. These results for Nd(III), Cm(III), Zr(IV), Th(IV), Pu(IV) and first results on the solubility of pentavalent Np(V) (all data obtained under carbonate-free conditions) indicate that the stabilization of anionic hydroxide complexes with unusual great numbers of OH⁻ ligands by association of Ca²⁺ ions is not a specific but a general phenomenon.

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A more realistic approach to speciation based on the Stability Constants Database

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The IUPAC Stability Constants Database (SC-Database) provides the most complete and accessible route to finding stability constants in the literature. However, in the real world, literature values must be treated with caution. The structure of the database, and the means of access, will be described. From the point of view of collecting important and significant constants SC-Database is approaching the completion of its task, which is scheduled for 2009. What is required now is the accurate measurement of constants for a number of important systems, particularly with inorganic ligands.

Stability constants are measured and reported with varying degrees of accuracy and rigour, and under varying experimental conditions. Methods of using these constants to correct for ionic strength changes and temperature, and to reflect possible error in calculated speciation curves, are now being developed.

Uncertainty in speciation calculations: Historically speciation curves have always been drawn as sharp lines. These could only result from knowledge of the exact stability constants, using the exact model for the system. Errors are never included. Unfortunately published stability constants give errors in unpredictable ways and do not include correlation coefficients. Two approaches to compensating for these limitations will be considered.

1. If realistic standard deviations (σ values) are known, a '*Monte Carlo*' approach to allowing for these deviations could be made. For systems with more than a few significant species this rapidly becomes too slow, even on fast PCs. Graphical display of calculated curves presents additional software problems. Results for simple systems (e.g. $nH + L$ and $HL + M$) will be shown.

2. Possible errors become even greater with more complicated (and important!) systems, e.g. Al^{3+} hydrolysis when poly-ions such as $Al_{13}(OH)_{32}^{7+}$ are formed before $Al(OH)_3$ is precipitated. The effect of these errors may be treated by ignoring errors in other constants and software to demonstrate the effects will be presented.

Ionic strength corrections: Specific Ion interaction Theory (SIT) is the most general method of compensating for ionic strength changes up to about 5 M. The latest version of our SIT program will be demonstrated. It may be used to calculate very precise values for K_w and other important constants in a variety of media.

Ways of representing graphically the dependence of stability constants on changes in conditions will be explored. Programs have also been developed to apply Pitzer parameters where they are available. These are particularly significant in sea-water and other natural waters.

Temperature corrections: A program will be available for correcting for temperature changes using 7 different equations.

Surface Complexation and Proton Promoted Dissolution in Aqueous Apatite Systems

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Apatites ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$) are the most abundant phosphorus-bearing minerals in nature. They are very important in agriculture as phosphorus containing fertilisers, as well as in medicine as main constituents of mammalian bones and teeth enamel. Surface layers of hydroxyapatite have been suggested to have a composition that is different from the bulk. This change is caused by a creation of vacancies on Ca and OH sites and the protonation of phosphate groups. The range of composition may be expressed as $\text{Ca}_{(10-x)}(\text{HPO}_4)_x(\text{PO}_4)_{(6-x)}(\text{OH})_{(2-x)}$. It thus seems important to characterize these surface layers in order to be able to interpret not only surface complexation reactions but also different types of dissolution processes.

The surface chemistry, in terms of surface complexation models, of apatite minerals is very much unexplored, and the dissolution mechanism is still debated. The objectives with our apatite studies are to characterize possible surface phase transformations and to clarify surface acid/base properties, ion exchange and readsorption reactions involving phosphate, calcium and fluoride.

The strategy in modelling surface complexation and dissolution of apatite is to yield information provided by different macroscopic techniques: i) potentiometric pH measurements; ii) dissolution characteristics with respect to soluble fractions of calcium, phosphate and fluoride; iii) readsorption studies of phosphate, fluoride and calcium, as well as iv) surface charge measurements. Furthermore, this information is combined with surface spectroscopic characterizations using FTIR, XPS and NMR methods. The presentation will highlight similarities and differences found in the hydroxyl- and fluorapatite systems.

Solubility and Critical Phenomena in Reactive Liquid–Liquid Systems

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The aim of the report is to present and to discuss some theoretical aspects and experimental results on the study of solubility in liquid-liquid systems for the case of equilibrium and non-equilibrium chemical reaction in liquid phases. The special aim is to consider the critical phenomena in these systems and peculiarities of diagrams of reactive ternary and quaternary liquid – liquid system. For the description of critical phenomena we use the approach that was previously developed for non-reactive systems. The main idea is the transformation of the stability matrix in the vicinity of critical states. According to this approach we could reduce the number of thermodynamic variables that are necessary for the analysis of the critical states and to present the results of critical properties consideration in compact and proper forms. For example the classification of critical points of ternary systems could be developed on this base. In present paper we also consider some singularities for critical points and curves both for non-reactive and reactive systems. The topology of liquid – liquid phase diagrams in the case of chemical reactions are also considered in general.

The experimental data base on the critical states in liquid – liquid reactive systems is rather poor. One of the practically important types of such systems is systems with esterification reactions. Due to usual immiscibility of water and esters such quaternary systems (acid – alcohol – ester – water) has the area of limited solubility in the composition tetrahedron. The experimental object of our research is a quaternary system with *n*-propyl acetate synthesis reaction. The solubility and liquid – liquid tie-lines in acetic acid – *n*-propanol – water – *n*-propyl acetate system were determined by cloud-point techniques method with the use of gas chromatography analysis. The location of the critical curve of liquid – liquid equilibrium in composition tetrahedron was determined. According to our experimental results for some areas of composition tetrahedron the liquid–liquid envelop and the surface of chemical equilibrium are located close to one another. Moreover we determined that the region of their intersection exists: such intersection of two surfaces corresponds to the curve in the tetrahedron with two critical points. In this report we also consider another data for systems with esterification reaction and liquid phase splitting including peculiarities and topology of phase diagrams.

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ORALS

Liquid-liquid Equilibrium in Quaternary System [bmim][PF₆] + Water + 1-Methylimidazole + 1-Chlorobutane

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Recent focus on ionic liquids as new, possibly greener, and more efficient class of solvents has led to an increased interest in their thermodynamic properties, primarily their phase behaviour in multicomponent mixtures. Phase equilibria are of essential importance e.g. in the design of industrial separation processes such as distillation and extraction.

In this work, liquid-liquid equilibrium in the quaternary system 1-butyl-3-methylimidazolium hexafluorophosphate (abbr. [bmim][PF₆]) + water + 1-methylimidazole + 1-chlorobutane was studied in order to investigate the extraction of the ionic liquid after its synthesis from the reaction mixture containing 1-methylimidazole and 1-chlorobutane. Experimental liquid-liquid equilibrium data were obtained by means of the cloud-point¹ and direct analytical methods, the former enabling us to determine regions of partial miscibilities, the latter providing us with compositions of the equilibrium phases. Concentrations of the individual components in the equilibrium phases were determined by gas chromatography for 1-chlorobutane and 1-methylimidazolium, UV/VIS spectroscopy for the ionic liquid and water contents was determined by Karl-Fischer titration.

The studied quaternary system appears to consist of three partially and three completely miscible binary subsystems, and four ternary subsystems presenting heterogeneous regions. The quaternary system presents both a two-phase and a three-phase region.

The acquired experimental data were subsequently correlated by the NRTL equation² using a gnostic regression method¹ and taking into account the chemical reaction 1-methylimidazole + 1-chlorobutane → 1-methyl-3-butylimidazolium chloride.

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Hydrated and similar melts in the ternary systems consisting of water and two electrolytes at room temperature.

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Attention has been devoted to systems, in which under laboratory temperature a liquid phase can be produced by mixing two crystalline phases. The conditions leading to such phenomenon have been discussed and in the case of such systems containing $\text{Li}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ the hydration analysis has been performed on the respective crystallization branches. To support the idea that such phases are rather melts than solutions, the complete melting points diagram in the $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ – $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ system has been presented. Several examples of similar behavior at the section with zero contents of water are given.

Solubility and Adsorption in Antimony Environmental Fate: the Case of the Goesdorf Mine, Luxembourg

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The environmental behaviour of antimony has received a lot of attention in recent years. As a consequence, many aspects of its environmental fate are progressively better understood. However, some aspects remain controversial. For instance, while it is generally accepted that antimony behaves conservatively in aquatic systems, thus implying a weak or negligible sorption on organic matter and mineral particles, most studies have shown that it has a low mobility in soils. This reduced mobility has often been associated to significant sorption to solid phases which would be in contradiction with the accepted behaviour in aquatic systems. Furthermore, there are also studies that show high mobility of antimony in soils. This communication will include two aspects. First, existing field evidence of antimony sorption on solid phases, mostly based on the application of extraction procedures, and published laboratory studies on antimony sorption by synthetic and natural mineral phases will be critically presented and discussed. Consensus and discrepancies will be outlined. Secondly, on the basis of the existing knowledge, results from an abandoned antimony mine (Goesdorf, Luxembourg) will be discussed. These results have been obtained by the application of different methods: antimony determination in water draining the mine adit by ICP-MS and voltammetry; characterisation of the mineralised vein by XRD; characterization of colluvial sediments and iron and manganese concretions by TEM-EDS, XRD and IR; speciation of Sb in the solid phase by sequential extraction and EXAFS. The role in antimony attenuation of solubility and adsorption on solid phases, mainly on iron oxyhydroxides, will be particularly discussed.

Thermodynamic Analysis of Solubility Measurements on Sparingly Soluble Ionic Solids with Basic Anions

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The solubility of sparingly soluble ionic solids with basic anions, such as metal oxides, hydroxides, basic salts, sulphides and carbonates, in water is thermodynamically characterized by the solubility product. Hydroxides, for example, of divalent metals dissolve according to



The equilibrium constant of this dissolution process is called solubility product:

$$K_s^\circ = a(\text{M}^{2+}) \cdot a^2(\text{OH}^-),$$

it is connected to the standard molar Gibbs energy and the standard molar enthalpy of reaction (1), respectively, by

$$\Delta_{\text{r1}}G_m^\circ = -RT \ln K_{\text{s0}}^\circ \text{ and } \Delta_{\text{r1}}H_m^\circ = RT^2 \left(\frac{\partial \ln K_{\text{s0}}^\circ}{\partial T} \right)$$

The determination of the solubility product is in principle a straight forward method to evaluate the standard molar Gibbs energy of formation and the standard molar enthalpy of formation.

$$\Delta_{\text{f}}G_m^\circ(\text{M(OH)}_2, \text{cr}) = \Delta_{\text{f}}G_m^\circ(\text{M}^{2+}, \text{aq}) + 2 \Delta_{\text{f}}G_m^\circ(\text{OH}^-, \text{aq}) - \Delta_{\text{r1}}G_m^\circ$$

$$\Delta_{\text{f}}H_m^\circ(\text{M(OH)}_2, \text{cr}) = \Delta_{\text{f}}H_m^\circ(\text{M}^{2+}, \text{aq}) + 2 \Delta_{\text{f}}H_m^\circ(\text{OH}^-, \text{aq}) - \Delta_{\text{r1}}H_m^\circ$$

For a methodological review of the experimental determination of solubilities of sparingly soluble ionic solids in aqueous solutions see ref.¹

Two prerequisites for obtaining reliable thermodynamic data from solubility measurements *i.e.* solubility products will be discussed.

- (1) The solid phase should be synthesized and characterized properly before and after the solubility measurement.

Case study: basic tin(II) chloride, $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$, abhurite.

- (2) Effects of particle size on solubilities should be considered. The dissolution behaviour of nanodispersed particles is of current research interest. Case study: nickel hydroxide, $\beta\text{-Ni(OH)}_2$, theophrastite.

¹H. Gamsjäger, E. Königsberger. *Solubility, of Sparingly Soluble Ionic Solids in Liquids*. In G. T. Hefter and R. P. T. Tomkins(Eds). *The Experimental Determination of Solubilities*. Wiley, Chichester, UK (2003), pp. 315-358.

Estimation of vapor liquid equilibrium of binary systems ethanol +1-hexanol and tert -butanol+1-hexanol using artificial neural network

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Vapor-liquid equilibrium (VLE) data are important for designing and modeling of process equipment. Since it is not always possible to carry out experiments at all possible temperatures and pressures, generally thermodynamic models based on equations of state are used for estimation of VLE. In this paper, an alternate tool, i.e. the artificial neural network technique has been applied for estimation of VLE for the binary systems viz. tert-butanol+1-hexanol and ethanol +1-hexanol^{1,2}. The temperature range in which these models are valid is 353.2-458.2K at atmospheric pressure. The average absolute deviation for the temperature output was in range 2-3.3% and for the activity coefficient was less than 0.009%.

1 H. Artigas, C. Lafuente, M.C. Lopez, F.M. Royo, J.S. Urieta, *Fluid Phase Equilib.* 134 (1997) 163.

2 H. Ghanadzadeh, A. Ghanadzadeh, R. Sariri and A. Boshra, *Fluid Phase Equilib.* 233(2005) 123-

CRITICAL EVALUATION OF SOLUBILITY OF RARE EARTH METAL CHLORIDES IN AQUEOUS SYSTEMS (PART II)

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Partly based on achievements of the late Tomasz Mioduski

IUPAC project of collection, compilation and critical evaluation of solubility data of chlorides of Sc, Y, La and Ln in water and aqueous solutions, containing a second solvent, a salt or an organic compound, is finished. This communication relates some regularities as well as some specificity observed for binary and ternary systems containing these chlorides and water.

In case of binary systems (the chloride – water) the most reliable solubility results are selected and these values are further used to find smooth solubility equations in the form:

$$\ln\{x^v (1-x)^r (v+r)^{v+r} r^{-r} [1+(v-1)x]^{-(v+r)}\} = A + B/T + C\ln T + DT$$

where x is the solubility in mol fraction, r the number of water molecules in the equilibrium solid phase, v the number of ions produced upon salt dissociation, T the absolute temperature and A,B,C, D the constants obtained during fitting procedure.

Experience with the many systems shows that quality of the solubility data is very substantial, otherwise the equations may reflect some effects that are artificial (unexplained maxima, minima and inflections on solubility curves). Unfortunately, in the case of Sc, Y and Ln chlorides the precise and accurate data are quite seldom obtained. It is found that for the significantly scattered solubility data, a truncated form of the solubility equation (when $D = 0$) works much better. The corresponding binary phase diagrams (rare earth metal chloride – water) are of similar shape, however the stoichiometry of the hydrates and their peritectic or congruent melting temperatures are changing, not always regularly.

Some general features of the ternary systems are observed. An addition of hydrochloric acid makes a systematic decrease of the solubility whereas an addition of acetic acid does not practically change the solubility when it is expressed in molal scale. An addition of Zn, Cd, Cs and Rb brings about formation of double salts. Several organic compounds form complexes with rare earth metal chlorides. Remaining systems are of an eutonic type. In case of mixed rare earth metal chloride systems, ranges of solid solubility of these salts (in form of hydrates) depend in substance on the hydrate stoichiometry and ionic radius ratio of the metals.

Solubility Applications of the Theory of Near-Critical Dilute Solutions

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In the past 20 years, significant understanding has been gained about the thermodynamics of dilute solutions near the critical point of the solvent. Since the initial derivation of the basic relationships,¹ the theory has been exploited in a variety of areas, many of which relate to solubility.

In this work, we describe three areas in which these concepts have been fruitful for solubility-related problems. The first is for the description of Henry's constants for gases in liquids over a wide range of temperatures. In particular, we describe the successful correlation of Henry's constants for common gases in water up to high temperatures, with physically sound extrapolation behavior. Second, we describe a related application for the partitioning of solutes between vapor and liquid, as is important in the steam power industry. The most recent summary of these first two applications is given by Fernández-Prini et al.² Third, we describe the application of the same fundamental principles to the description of the solubility of solids in supercritical fluids, where the original idea of Harvey³ has been successfully implemented and extended by the group of Teja.⁴

¹ Japas, M. L.; Levelt Sengers, J. M. H. *AIChE J.*, **1989**, *35*, 705.

² Fernández-Prini, R.; Alvarez, J. L.; Harvey, A. H. *J. Phys. Chem. Ref. Data*, **2003**, *32*, 903.

³ Harvey, A. H. *J. Phys. Chem.*, **1990**, *94*, 8403.

⁴ Méndez-Santiago, J.; Teja, A. S. *Fluid Phase Equilib.*, **1999**, *158-160*, 501, and subsequent work..

What Dielectric Spectroscopy Can Tell Us About Electrolyte Solutions

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Dielectric relaxation spectroscopy (DRS) measures the complex dielectric response of a sample to an applied oscillating electric field in the microwave (GHz) region as a function of the field frequency. The basic methodology of DRS was developed over 50 years ago but the technique has been largely ignored by solution chemists. Making use of advances in measurement and related technologies, modern DRS can provide unique insights into the nature of electrolyte solutions, especially in relation to the formation of solvent-separated and contact ion pairs. In many cases DRS can provide detailed information about the thermodynamics, kinetics and sometimes even structures of ion pairs. Analysis of the solvent contributions to DR spectra yields data on the solvation of the ions. This talk will briefly describe modern DRS, and its capabilities for understanding the nature of electrolyte solutions will be illustrated using recent measurements from the authors' laboratories.

Solubilities and Densities in the $\text{TiOSO}_4\text{--FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ System

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The sulfate process for titania (TiO_2) production involves leaching of ilmenite (ideal composition FeTiO_3) in sulfuric acid, followed by reduction of Fe(III) and precipitation of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$. Finally, the acidic solution of titanyl sulfate is decomposed hydrolytically to form titania.

Accordingly, the solubilities of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{TiOSO}_4\cdot 2\text{H}_2\text{O}$ in sulfuric acid solutions are key process parameters. The densities of such plant liquors are also important for process control and engineering design purposes. In particular, density is needed for the conversion of concentration units, e.g. from the frequently reported mass-based units (%) to the industry-preferred unit, g/L. Also, volumetric properties of solutions are required to calculate the variation of other thermodynamic quantities as a function of pressure.

In this presentation, the results of solubility and density measurements for the title system are reported and strategies for modelling these properties are discussed.

Purely empirical models for the correlation of physicochemical properties are highly susceptible to parameter correlation and consequent error propagation. Extrapolations beyond the range of data used in their parameterization must accordingly be made with considerable caution.

More fundamental models thus start from accurate, semi-empirical descriptions of the solvent and the constituent binary systems (in the present case, one electrolyte plus water). Properties of the multicomponent system are then predicted by simple, linear chemical 'mixing rules' that are well established experimentally for various physicochemical properties of mixtures.

However, acidic leach liquors may reach high acid concentrations in certain stages of the refinement process. The prediction of properties of mixed solutions by the mixing rules mentioned above requires knowledge of these properties for the binary (salt) solutions at high supersaturation. This is an aspect which has often been overlooked in the literature.

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PHREEQC modelling of metal speciation in metal-contaminated soils amended with chelating agents and chlorides: Implication for phytoextraction

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Enhanced phytoextraction of metals (e.g., Pb, Cd, Cu) from contaminated soils using various mobilising agents is a fast emerging method of soil remediation. However, the competition of other metals present in soils at high concentrations (e.g., Fe, Ca) lowers significantly the extraction efficiency. Therefore, high concentrations of the mobilising agents must be used which influences the costs of the phytoextraction process. This work focused on the phytoextraction of Pb, the main contaminant present in agricultural soils originating from the mining and smelting area of Příbram, Czech Republic. Batch incubation and pot experiments together with speciation equilibrium modelling using PHREEQC-2 were performed in order to evaluate the extracting efficiency of the tested mobilising agents (EDTA, NH_4Cl) and the possible competition of other metals present in the soils. The plants used for the pot experiments were maize (*Zea mays* L.) and hybrid poplar (*Populus* spp.). The results showed that Fe influenced greatly the extraction of Pb using EDTA, due to the ability of EDTA to slowly dissolve soil Fe-(hydr)oxides and to form stable Fe(III)EDTA complexes. Furthermore, the possible dissolution of Mn-(hydr)oxides by EDTA could influence the EDTA extraction as well. These results were confirmed by pot experiments. The addition of NH_4Cl increased the solubility of Cd and Zn, mainly because of the formation of highly mobile CdCl^+ and ZnCl^+ complexes. However, Pb was present predominantly as negatively charged PbCl_3^- , which led to sorption of the complex at lower pH values. The results obtained were in good agreement with pot experiments. Therefore, speciation modelling at equilibrium can help to better understand the metal extraction process and to minimise the costs of (phyto)extraction.

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IONIC LIQUIDS: THEIR SOLUBILITY AND POTENTIAL USE AS AGENTS IN SEPARATION PROCESSES.

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IONIC LIQUIDS have the advantage that a desired solubility can be tailor made by judicious choice of alkyl chain length, anion and cation type. Being ionic in nature they have the potential for separating polar compounds from mixtures containing non-polar compounds. For example they have the potential to separate alkanes, alkenes, aromatics and oxygenates from their mixtures. The separating power of an ionic liquid depends on the disparity in solubility of the IL between the compounds being separated. This paper will highlight the wide range of properties that ionic liquids have, for use in separation processes. Examples include imidazolium, pyridinium, pyrrolidinium and phosphonium ionic liquids. It will also highlight some of the negative aspects.

Recent results by our group and other researchers, show how very difficult it is to predict the potential of ionic liquids in Solvent Extraction and in Extractive Distillation processes. Never the less there are some potentially useful ionic liquids that may have properties superior to the presently used compounds such as Sulfolane, NMP, glycols etc.

Ionic liquids do have one very special property and that is a very low vapour pressure. This is such an important property in industrial chemistry that it is worth persevering and finding ionic liquids which do have the desired solubilities to be useful separating solvents.

THE PHASE RELATIONSHIPS AND DIELECTRIC PROPERTIES OF AQUEOUS POLYMER -SALT SYSTEMS USED IN THE SYNTHESIS OF NEW MATERIALS

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The aqueous compositions on the basis of water-soluble non-ionogeneous polymers (polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) and so on) and salts of various metals are used for synthesis of complex oxide materials. Their application as precursor demands the studying of phase equilibriums, processes of complex formation and salvation of ions, and also the molecular-kinetic state of water in these compositions. Systems ammonium heptamolybdate - water - PVA (or PVP) were choose as model systems for such researches.

The areas of homogeneous water - polymer -salt solutions, the solid solutions on the basis of polymer and the bi- and three-phase areas containing liquid and (or) solid phases (aqueous solution and a solution on the basis polymer and salt) are found on the isothermal sections of phase diagrams of systems PVA (or PVP) - ammonium heptamolybdate (AHM) – water. In system with PVP it is revealed the melting of crystalline molecular polymer-salt complex and the presence of liquid stratification with the lower critical point on phases, enriched accordingly polymer and salt. The molecular -kinetic changes in solutions of systems PVA -water (I), PVP -water (II), ammonium heptamolybdate - water (III) and sections ternary system ammonium heptamolybdate - PVA - water (IV) in all area of homogeneous water-polymer-salt solutions with constant concentration PVA or AHM were studied by means of microwave dielectric spectroscopy. The measurements of dielectric permittivity (ϵ') and losses (ϵ'') were carried out at frequencies range 13-25 GHz by method of dielectric rod in a wave-guide. The specific conductivity for calculation of ionic component of losses was studied too. Measurements are executed in temperature intervals 288-308 K for (I, II), 283-313 for (III) and 298-313? for (IV). Frequency dependence of complex dielectric permittivity has been analyzed with use of Cole-Cole relaxation model. The values of static dielectric constant (ϵ_s), describing hydration processes, and dielectric relaxation time (τ), connected with the change of the molecular-kinetic state of water molecules in solutions were found. It is established, that the change of rotatory mobility of water molecules in solutions of ternary system is defined mainly by effect of PVA on H-bond net. The method of the analysis of additivity of contributions to the change of dielectric constant in ternary system from data of ϵ_s for solutions of the double systems was used for the analysis of hydration and complex formation. Earlier it was applied to ternary water-salt systems. It is shown, that observable changes of ϵ_s in ternary system PVA- AHM- water are practically additive in relation to double systems PVA –water and ammonium heptamolybdate - water. Thus, it is possible to conclude, that in considered ternary system is not observed effects of mutual influence of components on hydration and a molecular-kinetic state of water molecules in solutions.

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SOLVATION AND TEMPERATURE DEPENDENCIES OF JOINT CRYSTALLIZATION AND SALT SOLUBILITY

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One of the main questions is how our knowledge of solvation and solvent structure in liquid phase may be used for understanding, classification and predicting the heterogeneous processes in the double and multicomponent systems and technological objects.

The relationships of phase salt diagrams with solvation thermodynamics and solution structure are investigated. A general approach is created. Above mentioned dependencies are considered on molecular level on the basis of known thermodynamic equations for temperature coefficients of solubility and joint crystallization on partial enthalpy effects. Assuming the division of these values into components corresponding to the molecular interactions in the solid phase and solution (the parts of solvation, complex formation, structural changes of solvent) we analyzed the changes of phase equilibria in aqueous, mixed and nonaqueous solutions of different salts.

The structural model of aqueous solutions of electrolytes in a wide concentration range (including saturated and multicomponent systems) is developed. The model is based on a principle of complementary organization of the first coordination sphere, intermediate layer and tetrahedral bulk water in the first concentration area and complementary organization of hydration shells and ion or (and) ion-water complicated forms in the high concentrated solutions (without broken intermediate layers). This model is used for comparison of aqueous and nonaqueous systems, estimation of thermodynamic parameters and their changes with temperature, pressure and concentration of salts. The higher the degree of solvation interaction for ions and ion complex forms and the smaller the variation in solution structure during ion implantation - the lower the temperature coefficient of solubility. These limit correlations found by us are confirmed by the data for ~200 systems. A classification of temperature dependencies of salt solubility is given on the basis of molecular scheme. The method proposed can be used to identify the common peculiarities of topology of polythermes of salt solubility in aqueous, mixed and nonaqueous solutions as well as the patterns of their relative variations in a number of salts. Also, it makes possible to suggest a general classification of temperature dependencies of salt joint crystallization and predict sign of temperature coefficient using data about hydration of ions of micro- and macrocompounds. The hydration of ions was determined using the static dielectric constants of concentrated electrolyte solution (from high frequency dielectric data).

In the limiting case for the distribution coefficient D : $\delta D/\delta T < 0$, if $R_{\text{micro}} > R_{\text{macro}}$ (R – radius of ions of macro and microcompounds). This model is supported by experimental results (38 examples). It is examined using literature data and own data for the multicomponent systems. The distribution coefficient of joint crystallization of ion Sr^{2+} with BaNO_3 in water-glycerol and water-*i*-propanol mixtures are investigated.

Thus, the considered changes of phase equilibria of nonelectrolyte-electrolyte systems mainly are determined by molecular interactions in solution, but not in solid phase. General differences between aqueous and nonaqueous systems are found.

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The Solubility of Whitlockite ($\text{Ca}_9\text{MgH}(\text{PO}_4)_7$) at 298.15 K

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Whitlockite is a mineral with the chemical formula $\text{Ca}_9(\text{Mg},\text{Fe}^{2+})(\text{HPO}_4)(\text{PO}_4)_6$ but it is also used to refer to synthetic solids with the chemical formula $\text{Ca}_3(\text{PO}_4)_2$, which can only be obtained by solid-state reactions at temperatures higher than 800 °C. Whitlockite is also a biomaterial that can be found in dental calculi, salivary stones, caries-free human tooth enamel, and crystallized on the tooth surface under tooth calculi during the enamel caries process, and at extra- or intratissular sites as in urinary calculi, aortic valvular topchi, arthritic cartilage and non-infectious diseases of bone tissue¹. Whitlockite permits some variations in the Ca/Mg ratio without changes in the structure. There are different values proposed for the maximum magnesium incorporation in the whitlockite structure that ranges from 9.5 cation % of magnesium for a solid with the composition $\text{Ca}_{19}\text{Mg}_2(\text{PO}_4)_{14}$ to around 16 cation %. Biological whitlockites contain no iron, and slightly lower magnesium than the maximum magnesium substitution obtained for synthetic materials¹. Crystallization of whitlockite occurs under given values of pH independently of the Mg/Ca and Ca/P ratios in the aqueous solutions. No solubility data for whitlockite are available in the literature. Accurate values for the solubility constant of whitlockite are still needed once in the literature was only found the value, $\log IP = -106.34$ obtained under non-equilibrium experimental conditions by Hamad and Heughebaert². This value is calculated from the chemical equation $\text{Ca}_9\text{Mg}(\text{HPO}_4)(\text{PO}_4)_6(\text{s}) + \text{H}^+(\text{aq}) + 9\text{Ca}^{2+}(\text{aq}) + \text{Mg}^{2+}(\text{aq}) + 7\text{PO}_4^{3-}(\text{aq})$. Synthetic whitlockite with the Mg/Cations ratio in the range [9.2 – 15.3 %] was obtained from aqueous solutions, under controlled pH and temperature. The solubility data were obtained from the synthetic solids-aqueous solutions equilibrium experiments. The solids were left in contact with their original mother aqueous solutions, at 298.15 K up to five weeks. The solids were characterized by ICP, infrared, X-ray diffraction and SEM. The solutions were analysed by ICP. The obtained value for the solubility constant of the solid with the ideal formula $\text{Ca}_9\text{MgH}(\text{PO}_4)_7$ was found to be in the $\log K_s$ range [-111.4 – -115.7] within 95 % confidence. The average value for the solubility constant was found to be $\log K_s = -112 \pm 4$. This value must be more accurate than the previously published by Hamad and Heughebaert² for the solubility ionic product of whitlockite..

1 Magalhães, M. C. F.; Marques, P.A.A.P.; Correia, R.N. Calcium and magnesium phosphates: normal and pathological mineralization, in Koenigsberger, E.; Koenigsberger, L-C. Biomineralization – Medical aspects of solubility; John Wiley and Sons, 2006. 2 Hamad, M.; Heughebaert, J.C. J. Crystal Growth, 1986, 79, 192.

Preferential Solvation of Drugs in Solvent Mixtures

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Most studies of the solubility of drugs in solvent mixtures have as their purpose the modeling of the solubilities in terms of the solvent composition, possibly also the prediction of the solubilities in the mixtures from those in the pure components. A very recent example is the study by Manrique et al.¹ of the solubility of ibuprofen (IBP) and naproxen (NAP) in aqueous 1,2-propanediol (PG) at several temperatures.

Thermodynamic functions of the solvation of the drugs were obtained, but not how they are preferentially solvated by water and by PG. A recent study of the present author² showed that such information can be obtained by the application of either of two approaches, the inverse Kirkwood-Buff integral (IKBI) and the quasi-lattice quasi-chemical (QLQC) ones. Their use depends on the quality of the solubility data and the availability of required auxiliary data, such as the excess Gibbs energy of mixing of the components of the solvent. The results, given as the composition of the solvation shell of the drug molecules, relates to the interactions of these molecules with those of the solvent components.

These approaches are here applied to the preferential solvation of IBP and NAP in H₂O + PG, and the interactions involved are deduced. These are compared with the conclusions of Manrique et al.¹

1. Manrique, Y. J.; Pacheco, D. P.; Martinez, F. J. *Solution Chem.* (2008) **37**, 165.
2. Marcus, Y. J. *Mol. Liq.* (2008) **140**, 61.

Determination of Gold by Electrothermal Atomic Absorption Spectrometry after single drop Microextraction

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Due to the importance of gold and their extremely low levels various matrices, highly sensitive and rapid methods required for its trace and ultra trace determination. In trace element analysis, preconcentration and separation methods enhance the sensitivity and precision of the determination. In this work we describe a high sensitivity method for extraction and determination of gold in aqueous samples by liquid phase microextraction combined with a graphite furnace atomic absorption spectrometry. For obtaining higher sensitivity we applied method of "single drop microextraction" for determination of trace amounts of gold. In this method Au is reacted with Orthophenylen 2-mercapto aniline, the complex formed was then extracted into micro drop of 1,2 dichloroethane. After extraction, the micro drop was retracted and directly transferred into a graphite tube modified by $[Pd_{(c)}+Pd_{(i)}]$. The detection limit was calculated to be 0.8 $\mu\text{g/l}$ (absolute value of 0.3 ng) based on $3S_b$. The relative standard deviation for five replicate analysis of 10 $\mu\text{g/l}$ Au was 6.5%. The calibration curve was linear in the range of 0.8 to 40 $\mu\text{g/l}$ with a sensitivity of 0.25 $\mu\text{g/l}$.

Effects of Basic Slags on Soil Properties and Plant Biomass in a Trace Element-Contaminated Soil

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Basic slag (BS) containing 30.9 % Calcium (Ca), 4.2 % Silicon (Si), 7.3 % Iron (Fe) and 1.1 % Magnesium (Mg) is a by-product of the steel industry. Such compound is a potential liming source able to improve physical and chemical soil properties, to change availability of trace elements in soil and metal and metalloid uptake by plants (Dual effect).^{1,2,3} The effects of (BS) on soil properties and plant biomass were investigated in soil contaminated by trace elements (Cu, As). The soil collected in the 0-25cm depth layer was strongly Cu-contaminated due to former activities of wood treatment using solutions of Cu sulphates and chromated copper arsenate.⁴ The pot experiment was carried out with dwarf beans (*Phaseolus vulgaris* L.) grown on the contaminated soil. The ameliorative materials were added into the pots (1 kg soil) at the following rates: 0 %, 1 %, 2 % and 4 % of BS/kg soil. The (BS) incorporation has a positive effect on soil pH, soil conductivity (EC) and plant growth compared to the untreated soil. The basic slag treatments increased soil pH in relation with the addition rate, from 5.64 in the untreated contaminated soil to 7.9, 8.3 and 9.8 in the soils amended at 1%, 2% and 4 % basic slag addition rate. Soil pH in an uncontaminated control soil was 7.0. The basic slag incorporation increased soil (EC) from 147.2 $\mu\text{S}/\text{cm}$ in the untreated soil to 389, 466 and 821 $\mu\text{S}/\text{cm}$ in the 1%, 2% and 4% slag basic treated soils respectively. Soil (EC) was 624 $\mu\text{S}/\text{cm}$ in the control soil. Treatments with 1% and 2% basic slag addition rate resulted in the highest shoot yields (fresh and dry weight) and a higher water content in the shoots of beans. The concentrations of Cu in the shoots ranged from 6.09 to 53 mg/kg whereas total Cu concentration in the soil was 630 mg Cu/kg. Data demonstrated that in this contaminated soil, Cu availability and soil phytotoxicity can be reduced with the incorporation of a basic slag into the soil. The concept of dual matrix effect dedicated to trace element-contaminated soil is discussed.

¹ Pinto, M.; Rodriguez, M.; Besga, G.; Lopez F.A. 1995. New Zealand. J. Agric. Res. 38.

² Besga, G.; Pinto, M.; Rodriguez, M. 1996. J. Nut. Cyc. Agroecosystems. (46):157-167.

³ Barbosa Filho, M.P.; Zimmwrmann F.J.P.; Da Silva O.F. 2004. Cienciae Agro.28.

⁴ Mench, M.; Bes, C. 2006. 3^{ème} séminaire d'écotoxicologie de l'INRA, Dinard, France.

Molecular Orientation and Dielectric Anisotropy Properties of 4-cyano-4'-n-heptylbiphenyl-TiO₂ Liquid Crystal Composite

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The molecular orientation and the dielectric anisotropy of the nematic liquid crystal (LC) 4-cyano-4'-n-heptylbiphenyl (7CB) and of TiO₂-doped 7CB have been investigated. The dielectric properties of the LCs exhibit relaxation peaks that shift to lower frequencies with increasing voltages. The relaxation frequencies of the 7CB and 7CB/TiO₂ liquid crystals were found to decrease as the bias voltage increased. The dielectric anisotropy of the LCs changes from positive type to negative type and the static electric permittivity and dielectric anisotropy values were found to be lower for the 7CB/TiO₂ system.

Measurement of the Solubility of Various Metallic Divalent Carboxylates : Application to the Selective Precipitation of Metals Contained in Industrial Wastewater

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Chemical precipitation is the most common technology used to remove dissolved metals from industrial wastewater. The most widely used chemical precipitation process is hydroxide precipitation, in which metal hydroxides are formed by using calcium hydroxide $\text{Ca}(\text{OH})_2$. Most of metal hydroxides are amphoteric. Therefore, when a process wastewater contains mixed metals, the optimum pH for precipitation of one metal may cause another metal to solubilise. In addition, chelators or others bath additives will interfere with the reaction of hydroxide precipitation. As an alternative to hydroxide precipitation, numerous companies have developed and marketed chemical products which react with metal species to form insoluble compounds such as sulphides or carbamates. However, whatever the reagent used, chemical precipitation processes lead to sludge without any commercial or industrial values which are stored in specialized landfills. As example, surface finishing industry generates each year in France about 200.000 tons of metallic hydroxide sludge which undergo a solidification/stabilization process using hydraulic binders before storage.

The aim of this work was to study the possibility using sodium carboxylates as precipitant to perform selective precipitation of metals contained in industrial wastewater. These non-toxic compounds, derived from fatty acids extracted from vegetable oil and animal fats, form insoluble compounds with metallic cations.

First, metallic carboxylates were prepared and controlled before determining their solubility in pure water at 20 °C in order to calculate solubility products K_{sp} . Compounds prepared from seven cations (Cd^{2+} , Co^{2+} , Cu^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}) and four linear saturated carboxylates (heptanoate, octanoate, nonanoate, decanoate) were investigated. Additional measurements were performed with dodecanoate and octadodecanoate in order to study the influence of the carboxylate chain length on the solubility.

Using MINEQL+ software, solubility domain of each carboxylate was plotted and superimposed leading to a tool allowing predicting the feasibility of a separation. The reliability of this tool was verified performing different separations which were possible according their solubility curves.

Finally, selective precipitation was applied to different industrial mixtures: Ni^{2+} - Cd^{2+} (sulphuric leachates of Ni-Cd spent batteries), Zn^{2+} - Ni^{2+} (liquid waste coming from fume scrubbing), Zn^{2+} - Mn^{2+} (sulphuric leachates of Zn/MnO₂ spent batteries), Cu^{2+} - Zn^{2+} (spent brass plating baths).

The mechanism of adhesion of calcium carbonate on various kinds of solid surfaces

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Scale formation of CaCO_3 is often a major problem encountered not only in inorganic chemistry, geochemistry, and biomineralization but also in many industrial facilities such as heat exchangers, steam generation equipment, pipes, etc. Although the precipitation of calcium carbonate in the bulk solution has been intensively studied from the viewpoint of the nucleation and growth of crystals, significantly less information exists for the mechanism of scale formation on a solid surface.

We have reported the detailed mechanism for the formation and transformation of calcium carbonate precipitate in solution. That is, amorphous CaCO_3 (ACC) immediately precipitates from the highly supersaturated solution. ACC thus formed is transformed into crystalline CaCO_3 , calcite and vaterite, within 7 minutes (25 °C). The metastable polymorph, vaterite, is finally transformed to calcite. The scale formation of calcium carbonate was investigated by combining a Quartz Crystal Microbalance (QCM) technique with continuous measurements of the ion concentrations in solution. By taking into consideration the transformation of CaCO_3 in the bulk solution, the detailed mechanism of the calcium carbonate adhesion on the gold surface has been reported.

In the present study, in order to study the scale formation of calcium carbonate on various kinds of solid surfaces. From the viewpoint for the actual application to the piping, tubing, radiator materials, the scale formation on the surfaces of metals (steel, stainless steel, Cu, brass, Ni, Al, Pb), plastics (polyethylenes, polyvinyl chloride, acrylic resin) and glasses (soda glass, borate glass) have been studied. The general results are followings: When the solid plate was inserted in solution prior to ACC precipitation, only the calcite crystals nucleated on the surface and grew to large size. When the plate was inserted in solution just after the precipitation of ACC, vaterite crystals were simultaneously formed with the calcite. Calcite crystals gradually grew, whereas the vaterite crystals dissolved and finally disappeared. When the plate was inserted after the transformation of ACC into crystalline polymorphs in the solution, no calcium carbonate was formed on the surface. The amount, population and size of CaCO_3 adhered on the surface are predominantly ruled by the roughness of the solid surface. In case of relatively rough surface, micro size dimples of the surface play an important role for the nucleation of the crystal. The effect of etching and scratching of the plate surface on the adhesion will be discussed.

High-Pressure Solubility of Biphenyl in Water and Volume Change for Hydrophobic Hydration

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Logarithm of the solubility of biphenyl in water decreased with increasing pressure up to 370 MPa at temperatures 288, 298, and 328 K. From the slope, the volume change for dissolution, ΔV_{sol} , of biphenyl in water can be estimated to be $11.7 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$ at those temperatures using the equation:

$$\Delta V_{\text{sol}} = -RT[\ln(\text{solubility})/p]_T.$$

This ΔV_{sol} corresponds to the difference between V_w , *i.e.*, partial molar volume in water at infinite dilution and molar volume of solid biphenyl, V_s , that is, $\Delta V_{\text{sol}} = V_w - V_s$. Then, using $V_s = 130.8 \text{ cm}^3 \text{ mol}^{-1}$ from X-ray data of solid¹ and the ΔV_{sol} , we can obtain $V_w = 142.5 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$. (This value is never estimated from a usual method of aqueous density measurement because of low solubility of biphenyl in water. So high-pressure solubility is the sole method to estimate V_w of biphenyl.)

Our interest is in the volume change, ΔV_{hh} , for hydrophobic hydration defined as $\Delta V_{\text{hh}} = V_w - V_{\text{org}}$ where V_{org} is the partial molar volume in nonpolar organic solvents at infinite dilution. Since Kauzmann (1959), it has been believed that the sign of ΔV_{hh} is negative. Many measurements of the volumes have supported the situation; for example $\Delta V_{\text{hh}} = -1 \text{ cm}^3 \text{ mol}^{-1}$ for $-\text{CH}_2-$, and -4.1 , -5.0 , -8.5 , and $-8.5 \text{ cm}^3 \text{ mol}^{-1}$ for benzene, toluene, ethylbenzene, and propylbenzene, respectively³; suggesting that ΔV_{hh} decreases with increasing molecular weight of hydrocarbons. Recently we have measured positive values of $+1.4$ and $+4.1 \text{ cm}^3 \text{ mol}^{-1}$ for ΔV_{hh} of anthracene and phenanthrene, respectively, from the high-pressure solubility⁴. Further $\Delta V_{\text{hh}} = -0.1 \text{ cm}^3 \text{ mol}^{-1}$ for naphthalene⁵ means that ΔV_{hh} increases in the order of benzene ($-4.1 \text{ cm}^3 \text{ mol}^{-1}$), naphthalene ($-0.1 \text{ cm}^3 \text{ mol}^{-1}$), and anthracene ($-1.4 \text{ cm}^3 \text{ mol}^{-1}$) with increasing molecular weight.

ΔV_{hh} of biphenyl is estimated to be $-6.6 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$ ($= V_w - V_{\text{org}} = 142.5 \pm 1.5 - 149.1 \pm 0.1$) using $V_{\text{org}} = 149.1 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ which is the partial molar volume of biphenyl in CCl_4 as a nonpolar organic solvent measured in the present work using a vibrating densitometer. This value is smaller than that of naphthalene (or anthracene) and larger than twelve times of $-\text{CH}_2-$ ($12 \times (-1 \text{ cm}^3 \text{ mol}^{-1})$). Molecular diameters for the short distance as rotational molecules are 0.55, 0.62, and 0.74 nm for $-\text{CH}_2-$, biphenyl, and naphthalene, respectively. Such a relation suggests that the hydration structure of hydrophobic compounds depends on molecular size.

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Solubility of KNO_3 , K_2SO_4 and CuSO_4 in Water at Different Temperatures

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The solubilities of potassium nitrate, potassium sulphate, and copper sulphate in water were measured in the range between 293 and 343 K using an analytical gravimetric method. The reliability of the method was checked by comparing the experimental data with literature values. The method proved to be very accurate, and the solubilities are generally reproducible when compared to the data reported in the literature. The solubility studies of salt-containing systems are very important for many industrial applications. More particularly, knowledge of accurate solubilities is needed for the design of separation processes such as extractive crystallization¹ or for the safe operation of different processing units such as distillation columns, absorption units, and extraction plants.^{2, 3} The systematized experimental study implemented is an important contribution to the fulfillment of the great demand for salt solubility in aqueous solvent systems; a high number of experimental solubilities have been measured for the salts KNO_3 , K_2SO_4 and CuSO_4 in the pure water at different temperatures.

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Some General Features of Phase Behavior for Ternary Sub- and Supercritical Mixtures with One Volatile Component.

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There are three classes of ternary phase diagrams (**1-1-1**, **1-2-1** and **1-2-2**) for the systems with one volatile component, taking into account of two main types of phase behavior (types **1** and **2**) in binary subsystems in a vicinity of critical parameters of the volatile component. Such general features of binary phase equilibria as the different signs of temperature coefficient of solid solubilities and various types of immiscibility regions, an existence onexistence of critical phenomena in solid saturated solutions and the supercritical fluid equilibria are spreading into a three-component region of composition, intersect each other and form the main features of ternary phase behavior.

The following transformations of phase equilibria in ternary mixtures will be discussed:

1. a change the sign of a coefficient of solid solubility in ternary systems of classes **1-2-1** and **1-2-2**.
2. a disappearance of immiscibility regions of different types in ternary systems of classes **1-1-1**.
3. a transition of metastable immiscibility equilibria into the stable ones in ternary systems of classes **1-2-1** and **1-2-2**.
4. a heterogenisation of homogeneous supercritical fluid in ternary systems of classes **1-2-1** and **1-2-2**.
5. an appearance of nonvariant critical and noncritical equilibria in ternary systems of classes **1-1-1**, **1-2-1** and **1-2-2**.

The mentioned phase equilibria will be shown as the schemes of ternary phase diagrams and illustrated by the experimental examples of various systems consisted of the components of different volatility.

**The THEREDA database for modelling of solubilities in the hexary oceanic salt system
Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻ - H₂O**

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The project THEREDA¹ (Thermodynamic Reference Database) represents a German database project for performance assessment studies. It was started two years ago and is supported by the major German research institutions working in the field of radioactive and toxic waste disposal. The main objective of THEREDA is the generation of a comprehensive and internally consistent thermodynamic reference database for geochemical modeling of near-field and far-field processes occurring in repositories for radioactive wastes in different rock formations. THEREDA focuses especially on modelling of solubilities and reactions in aqueous media at ambient temperatures. It will cover thermodynamic data from an extensive list of systems and constituents:

- sea-water system H⁺- Na⁺- K⁺- Mg²⁺- Ca²⁺- Cl⁻- SO₄²⁻- CO₃²⁻- OH⁻- H₂O
- solution species of actinides Th, U, Np, Pu, Am, Cm Pa and fission products I, Se, Cs, Rb, Sr, Sm, Tc, Ra
- toxic metals consists of Cr, Co, Ni, Cu, Zn, Cd, Hg, Pb, As.
- cement phases and compounds

The main features of the database project are reviewed shortly. For the sea-water system solubilities were modelled on the basis of Pitzer's equations. A complete set of parameters is given for the title system valid from T = 0°C to 110°C, in some subsystems also to higher temperatures. Thus, it is now possible to simulate reactions and phase equilibria in solutions rich in MgCl₂ and other components of the hexary oceanic system. At the examples of solubility isotherms and solution compositions of invariant points at various temperatures the quality of the model and deficiencies in experimental data are discussed.

Literature:

¹ www.thereda.de

Flory-Huggins Interaction Parameters as a Function of Composition for the Systems Pullulan, Dextran and Cellulose plus Water

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Experimental information^{1,2} on the binary systems specified in the title was obtained at various temperatures by combining vapor pressure measurements (yielding data for high polymer concentrations) with the determination of light scattering or osmotic pressures (providing the limiting behavior for infinite dilution). These results demonstrate complicated composition dependencies of the Flory-Huggins interaction parameter χ . In the case of water/cellulose χ passes a distinct minimum¹ at a volume fraction of approximately 0.5. At high polymer concentrations $\chi < 0$, but it increases pronouncedly upon dilution in accordance with the limited miscibility of the components in this regime. Pullulan and Dextran are completely miscible with water, where pullulan interacts more favorably with water than dextran. In these cases the composition dependence of χ is particularly uncommon, exhibiting the concurrent appearance of two extrema, a minimum at moderate polymer concentration and a maximum at high polymer concentration.

In order to model these findings a previously established approach³, subdividing the mixing process into two clearly separable steps, was generalized² to account for specific interactions between water and the pullulan or dextran segments. Three adjustable parameters suffice to describe the results quantitatively; according to their numerical values the reasons for the solubility of polysaccharides in water, as compared with that of synthetic polymers in organic solvents, differ in a principal manner. In the former case the main driving force comes from the first step (contact formation between the components), whereas it is the second step (conformational relaxation) which is advantageous in the latter case.

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Dissolution enthalpy of polyhalite and its analogues

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Polyhalite $\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ is a common mineral in salt rock formations. The analogue triple salts, where Mg is substituted by Mn, Fe, Co, Ni, Cu, Zn have been prepared and characterized earlier¹.

In a next step the fields of crystallization from aqueous solutions shall be investigated. Since crystallization of polyhalite proceeds very slowly solubility was determined at 313 K. The combination with an activity coefficient model based on Pitzer's equations gives the possibility to estimate the crystallization fields at 298 K, presumed the heat of dissolution of the polyhalites is known.

With this aim calorimetric measurements of the heat of dissolution in NaClO_4 -solutions were performed at 298.15 K. NaClO_4 concentration was varied from 0.5 to 2.0 mol kg^{-1} .

All polyhalites dissolve exothermally. With increasing NaClO_4 concentration the integral heat of dissolution becomes more exothermic for all polyhalites. For extrapolation to infinite dilution the SIT model was used.

Within the limits of experimental uncertainty the enthalpies of dissolution for the triple salts $\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ with $M = \text{Mg, Mn, Co, Ni, Cu, Zn}$ coincide. The value for the cobalt salt is noticeable endothermic. Leightonite $\text{K}_2\text{CuCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, which crystallizes not in the polyhalite structure shows considerable differing dissolution enthalpies.

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Thermodynamic study of the system LiCl+NaCl+H₂O

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LiCl+NaCl+H₂O system is a main subsystem in the salt brines on the Qinghai-Tibet plateau in the west of China. The study of the thermodynamic activity properties for the ternary system in concentration range near solubility limitation is very lack, and the representation of the properties with standard Pitzer's ion-interaction model shows large deviations in previously literatures^{1,2}. On the other hand, there are some obvious differences among solubility isotherms of the system LiCl+NaCl+H₂O at 25°C reported by some authors³⁻⁵. While the formation of the double salt 2NaCl·LiCl·H₂O was reported in literature³, however, single salt and hydrate, NaCl and LiCl·H₂O, have only been detected by other authors^{4,5}. The concentration lines of these saturated solutions are also in disagreement. Thus, the measurements and representation of the thermodynamic properties of the system, including the water activity and solubility, are very necessary and significant.

In this article we have measured the water activities and osmotic coefficients for the systems LiCl +H₂O and LiCl+NaCl+H₂O at 298.15K by isopiestic method using improved isopiestic device. These measurements were extended from low molalities to near saturated solution molalities (from 0.1084 mol·kg⁻¹ to 16.0126 mol·kg⁻¹) for the LiCl +H₂O binary solutions and total molality range from 0.1034 mol·kg⁻¹ to 15.6919 mol·kg⁻¹ with eight NaCl molality fractions from 0.0025 to 0.75 for the ternary solutions, respectively. The experimental data are represented using an extended Pitzer's ion-interaction model. The model parameters were evaluated by fitting to the present experimental data and those from literatures with small standard deviations. Besides, the accurate concentrations of the saturated solutions for the ternary system in the high LiCl concentration region were measured. The solubility isotherms of LiCl+NaCl+H₂O system at 25°C were predicted using the extended Pitzer's ion-interaction model, which are in good agreement with the measurement results in this work. The solubility isotherms predicted were also compared with those in the literatures³⁻⁵, indicated that the isotherms in the literature⁴ may be more reasonable.

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Modification of a BET model for Multi-component system and its application in solubility phase diagrams containing highly soluble salts

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BET model derived by Ally and Braunstein [1] has been proved to be successful in description and prediction of thermodynamic properties of “ideal” multi-component aqueous systems containing highly soluble salts. However, the model fails for the systems when the salt-salt interaction gets ignorable. Based on the suggestion of Abraham and Abraham [2], that the interaction between salt can be expressed in a regular solution, we modify the above version of BET model and apply the modified model to a serial of multi-component systems containing highly soluble salts, i.e. LiCl-LiNO₃-H₂O, LiCl-CaCl₂-H₂O, LiCl-MgCl₂-HCl-H₂O, NH₄NO₃-LiNO₃-H₂O, and Mg(NO₃)₂-NaNO₃-LiNO₃-H₂O et al. With only two parameters for each binary salt-water system and one parameter for each ternary system, the modified BET model can describe the properties of the above multi-component systems perfectly, including the water activity and solubility. With the modified BET model, two room-temperature phase change materials has been predicted in the systems NH₄NO₃-LiNO₃-H₂O and Mg(NO₃)₂-NaNO₃-LiNO₃-H₂O, which has then been proved to be correct by experiments.

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How can Scheelite be digested by Caustic soda? Solubility effect on leaching process

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In the past two decades, leaching of scheelite concentrate by caustic soda solution has been widely adapted in commercial practice in china. But according to traditional thermodynamic analysis¹, it is considered that CaWO_4 can not be digested by NaOH solution. Here, a new thermodynamic explanation is given by a pseudo-ternary-system phase diagram method to show the effect of salt solubility on leaching. The phase diagram shows that under the condition of high NaOH concentration, the solubility of sodium tungstate becomes lower than the concentration necessary for keeping the reaction $\text{CaWO}_{4(s)} + 2\text{NaOH}_{(aq)} = \text{Na}_2\text{WO}_{4(aq)} + \text{Ca}(\text{OH})_{2(s)}$ at equilibrium. So, scheelite will be leached under the huge thermodynamics impetus and become soluble sodium tungstate. Correspondingly, the solution becomes supersaturated, and sodium tungstate crystal was precipitated constantly until scheelite disappears completely.

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Salt-forming Phase-diagram of $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ System in the Non-equilibrium State of Boiling Evaporate Process

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The non-equilibrium behavior of salt forming was experimentally determined for the system of $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ during evaporating. The experiments of evaporation were carried out at a constant boiling temperature of 100°C by a heating agent of fixed temperature of 140°C . The used evaporation intensity was about $140\sim 160\text{g}/(\text{h}\cdot\text{l})$. The compositions of liquid and solid phase were analyzed at the point of the occurring primary nucleation and the following points of further evaporating. According to the experimental results the Salt-forming Phase Diagram and the concepts of primary, extended and conditional salt forming region were proposed to express the behavior of salt forming in the Non-equilibrium process. The experimental results show that: (1) the primary salt forming regions of Na_2SO_4 , Vanthoffite, Loewite, $\text{MgSO}_4\cdot\text{H}_2\text{O}$ were observably different from those in Equilibria Phase Diagram. Based on the Jänecke index, the width of primary forming region of Na_2SO_4 is extended from 21.02 to 32.76, the width of primary forming region of $\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4\cdot 2.5\text{H}_2\text{O}$ is reduced from 41.40 to 25.71. (2) At the condition of having crystal seed, the width of salt-forming region is larger than that of primary salt-forming region in different degree for different salts, such as the region width of Na_2SO_4 and $3\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4$ increased by 7.72 and 8.81 respectively. The extend salt forming regions of each salt caused an overlap of adjacent phase regions. In the overlay region, what kind of the salt is formed depending on the seed of crystal. This overlay region is defined as conditional salt forming region, which is a special character in the non-equilibrium state phase diagram, and does not exist in the Equilibria Phase Diagram and Metastable Phase Diagram.

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Liquid –liquid Phase Diagrams of a Ternary System as a Function of Temperature: Water + 1, 4-Butanediol + 2-Ethyl-1-hexanol

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We have determined experimentally the liquid-liquid equilibrium of the ternary system water + 1,4-butanediol + 2-ethyl-1-hexanol at 298.15 , 303.15 and 308.15 K , using gas chromatography to gather with a calibration and the internal standard method. Further, we have studied the effect of temperature on the miscibility of 1, 4-butanediol with 2-ethyl-1-hexanol through the measurement of the phase diagram of the system water + 1, 4-butanediol + 2-ethyl-1-hexanol, at 298.15, 303.15 and 308.15 K. The experimental tie-line data obtained define the binodal curve of the studied system. The experimental tie-line data for the different ternary systems were correlated with NRTL and UNIQUAC solution models and plait points were derived ¹⁻³.

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Multinuclear NMR Study of Ligand Dissociation Equilibrium in Tin(IV) Complexes with Phosphine Oxides

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The solution structure of the octahedral complexes $\text{SnCl}_4 \cdot 2(\text{O})\text{P}(\text{NR}_2)_2\text{Cl}$ ($\text{R}=\text{Me}$ (**1**) or Et (**2**)) and $\text{SnCl}_4 \cdot 2(\text{O})\text{P}(\text{NR}_2)\text{Cl}_2$ ($\text{R}=\text{Me}$ (**3**) or Et (**4**)) has been investigated by multinuclear (^1H , ^{31}P and ^{119}Sn) NMR spectroscopy in dichloromethane solutions¹. The NMR data showed the presence of a mixture of cis and trans isomers for **1** and **2** and only the cis isomer for **3** and **4**. The dynamic behaviour of the complexes studied by variable temperature NMR indicated that the ligand dissociation equilibrium between the hexacoordinated and pentacoordinated tin species is much more pronounced for complex **3** and **4** than for **1** and **2**. The ligand dissociation equilibrium constants K_d for **1-4** were calculated. In dichloromethane solution, **3** and **4** are more fluxional. The fluxional process with values for ΔH_d of 1.56 (**3**) and 0.5 (**4**) kcal.mol^{-1} and for ΔS_d of -0.53 (**3**) and -0.76 (**4**) eu, involves considerably the complexes that show only cis configuration (i.e. complexes **3** and **4**). The results² are compared with those of the hexamethylphosphoramide complex.

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² Results to be published.

A Miraculous Freedom Degree of Evaporation: 1 or 0

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A new degree of freedom of isothermal evaporation process in complicated brine system, $f_e = n - r + r' - p$, in which n indicates total number of chemical constituent, p condensed phases, r concentration proportion relations retained in liquid, and r' dependent restrictions, respectively, has been proposed in the present paper. It is surprise that the conditional degree of freedom in dynamic process is extraordinarily simplified to either 1 or 0 and independent of the number of components and phases due to counteraction of internal variables. The Kurnakov's continuity and the unidirectionality of the process were concisely discussed. The significance of the findings was elaborated physically, geometrically and philosophically, respectively. The result shows that the process going forward refuses more degrees of freedom than 1 by reason of counteracting internal variables in the system, so that the system might become more succinct, more harmonious, more structured, and more symmetrical.

Liquid–liquid equilibria of (water + 2,3-butanediol + 1-Octanol) at several temperatures

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The importance of the availability of precise liquid–liquid equilibrium data (LLE) in rational design of many chemical processes and separation operations, have been the subject of much interest in recent years. Many researchers have investigated various kinds of multi-component systems in order to understand and provide further information about the phase behavior and the thermodynamic properties of such systems^{1,2}. In this work liquid–liquid equilibrium (LLE) data (water + 2,3-butanediol + 1-Octanol) were measured under atmospheric pressure and at different temperature ranges of 300.2, 305.2, 310.2, and 315.2 K. The UNIQUAC model was able to adequately represent the type I phase behavior observed over this temperature ranges in this ternary system. Using the experimental results, the values of the interaction parameters between each pair of components in the system were obtained for this model. The results obtained in this work were satisfactory and they were in accordance with root means square deviation (RMSD%). The root mean square deviation between the experimental and calculated mole percents was 6.26%.The mutual solubility of 1-octanol and water was also studied by addition of 2,3-butanediol at different temperatures.

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Liquid Phase Equilibria of(Water + 1,4- Buanediol + Cyclohexanol) Ternary system at Several Temperatures

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(Liquid- liquid) equilibrium (LLE) data are investigated for mixtures of (water + 1,4-butanediol + cyclohexanol) at 298.15 , 303.15 and 308.15 K and atmospheric pressure. The solubility curves and the tie-line end compositions of liquid phases at equilibrium were determined, and the tie -line results were compared with the data predicted by the NRTL method . The phase diagrams for the ternary mixtures including both the experimental and correlated tie-lines are presented. The distribution coefficients and the selectivity factors for the immiscibility region are calculated to evaluate the effect of temperature change. The reliability of the experimental tie-lines was confirmed by using Othmer -Tobias correlation¹. It is concluded that cyclohexanol may serve as an adequate solvent to extract 1,4-butanediol from its dilute aqueous solutions. The NRTL model correlates the LLE data for 298.15, 303.15 and 308.15 K with a root mean square deviation of 1.89, 2.46, and 2.69%, respectively, between the observed and calculated mole concentrations^{2,3}.

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Liquid-liquid equilibria of water + phosphoric acid + cyclohexane system

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Liquid-liquid equilibria (LLE) for the ternary system water + phosphoric acid + cyclohexane at 298.2 K are reported. A type 1 liquid-liquid phase diagram was obtained for this ternary system. The UNIQUAC model was used to correlate the LLE data with RMSD value of 1.05 %. The UNIQUAC interaction parameters between each pair of components in the system were obtained using the experimental results.

The importance of the availability of liquid-liquid equilibrium data (LLE) in the design of many chemical processes and separation operations, have been the subject of much interest in recent years. Many researchers have investigated multi-component systems in order to understand and provide further information about the phase behavior and the thermodynamic properties of such systems¹⁻³.

The PA content was analyzed by potentiometric NaOH titration in both the organic and the aqueous phases. And the water content of the organic phase was determined by titration with a Karl Fisher apparatus. The equilibrium compositions (fig. 1) The experimental data set was satisfactorily approved in the deviation test of thermodynamic consistency, using the UNIQUAC equation.

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Evaluation of Phase Equilibria in 12-Salt Six-Component Reciprocal Systems

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Studies of 12-salt six-component reciprocal systems are very important for deeper understanding of chemical, thermochemical, and energy processes in complex systems and for practical purposes.

This work, concerning chemical equilibria in melts, is the result of analysis of ten 12-salt reciprocal systems of different types, namely, Na,K,Ca,Ba//F,SO₄,WO₄ (2ABD Type); Na,K,Ca//F,Cl,SO₄,WO₄ (AC2D Type); Na,K,Ca,Ba//Cl,SO₄,WO₄ (4A Type); Na,K,Ca,Ba//F,Cl,WO₄ (AC2D Type); Li,Na,K//Cl,Br,NO₃,SO₄ (AB2C Type); Na,K,Ca,Ba//F,Cl,SO₄ (AB2C Type); K,Ca,Ba//F,Cl,SO₄,WO₄ (AB2C Type); Na,K,Ba//F,Cl,SO₄,WO₄ (3AD Type); Na,Ca,Ba//F,Cl,SO₄,WO₄ (3AB Type) и Na,Ca,Ba//F,Cl,SO₄,MoO₄ (3BC Type).

For each system mechanism of phase equilibrium forming is determined on the base of modeling. All systems are characterized by matrix, thermochemical, and geometrical models, including tables of vertex indices, sets of reaction stages, non-equilibrium and singular stars. Due to these models shift of exchange chemical equilibrium is determined in each system and properties of resultant products are predicted.

All systems under investigation can be divided into two groups depending on configuration of druse (nodule) of basic tetrahedra in the singular star cycle of the system. The base tetrahedra that are groups of four salts include all components of the system. These base elements consist of salts being a result of 18 exchange reactions between 12 salts. The systems of the first group have regular druse and the second group has irregular one. Configuration of the druse gives also a possibility to find out energy characteristics of this group of salts.

The fundamental aspect of the investigation is the discovery of the relationship between the base elements of the singular stars and their thermochemical and energy parameters.

In practical aspects discovered regularities may be used in experiment planning to chose compositions with the highest energy content for autonomous power sources, to determine process parameters (for preparing inorganic salts, rare metals, and alloys), to recycle industrial wastes, and for other purposes.

Determination of formation constants for iron-oxalate complexes in 0.1 M Na(Cl) ionic medium.

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Oxalate forms strong complexes with iron(III) in solution and on iron(III)-hydroxide mineral surfaces [1-3]. While the stability constants of the aqueous mono, bis and tris Fe(III)-hydroxide complexes have been determined previously in 1M ionic medium [4,5], to our knowledge there are no values reported in the literature for 0.1M ionic medium. Here, we determine these constants in 100mM Na(Cl) (constant sodium ion concentration). These data are to be used in a future study of the dissolution of goethite (FeOOH(s)) in this same ionic medium.

Model calculations were performed using Win SGW [6] that help understand the speciation of H⁺-oxalate and H⁺-oxalate-Fe³⁺ systems (with and without solid phase). Win SGW was used to design potentiometric titrations for the determination of formation constants. The stability constants of the HL⁻, H₂L, FeL⁺, FeL₂¹⁻, FeL₃³⁻ species in 0.1 M Na(Cl) ionic strength solution were calculated from titration data using MAGPIE [7] and LAKE [8] optimization tools. The values of the formation constants we determined are listed below:



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PURIFICATION PROCESS OF THE EFFLUENTS CONTAINING HEAVY METALS. APPLICATION OF THE SYSTEMES CADMIUM AND CHROMIUM

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The reactions for the extraction of cadmium from orthophosphoric acid are quite complicated because various of Cd(II) species may be present $\text{CdH}_2\text{PO}_4^+$, CdPO_4^- , HPO_4^{2-} , H_2PO_4^- and PO_4^{3-} in aqueous phase were taken into account in analysis of extractions. In this study, the mechanisms of extractions of cadmium from H_3PO_4 solutions with the oxide tri-n-octyl phosphine were investigated.

The reactions for the extraction of Chromium(VI) from sulphuric acid are also quite complicated, various of Cr(VI) species may be present. In this study, the mechanisms extraction of Cr(VI) from H_2SO_4 solution with the tri-n-octylamine were investigated

The process purification extraction - re-extraction would be particularly judicious in the case of treatments of the industrial wastes containing heavy metals; it is very sparing out of water and raw materials (recycling of the reagents and extractants)

Polymerization Equilibria of Phthalocyanine Derivatives Having Four Polyether Chains

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Because of their peculiar optical, magnetic and electrical properties, wide varieties of phthalocyanines (Pcs) and their metal complexes have been synthesized and studied as a new functional material. The polymerization (aggregation) of these compounds caused by the strong intermolecular interaction of the aromatic rings results in the reduction of the solubility and significant change in the optical properties such as fluorescence and absorption spectra. Consequently, increasing the solubility of the compounds and understanding of the polymerization behavior in solution are very important to control the functionality of phthalocyanines.

In the present paper, phthalocyanines substituted by four polyethers at β -positions having relatively long alkyl group (TDEO6-MPc, Fig. 1) were synthesized. These compounds are soluble in various kinds of solvents, from polar protic to non-polar aprotic, because of amphiphilic property of the polyether group. The UV-vis absorption spectra of the compounds were measured in various solvents at various concentrations. The solvent effect on dimerization of TDEO6-MPc has been investigated.

The polymerization equilibria of TDEO6-MPc were quantitatively analyzed by means of ^1H NMR spectroscopy. Dichloromethane was selected as the solvent because it is one of the most agreeable solvent to dissociate the compounds to monomer. The concentration dependence of chemical shift of each methylene proton was measured at wide concentration range ($10^{-6} - 10^{-2} \text{ mol dm}^{-3}$). The plots of chemical shifts as a function of logarithmic concentration of Pcs indicate the stepwise formation of polymers higher than trimer. These results were analyzed by non-linear least square method and the formation constants of polymers were evaluated. The structure of dimer of TDEO6-MPc was estimated from the chemical shift changes by the formation of polymer.

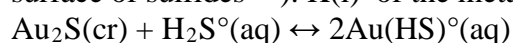
Fig 1. Structure of TDEO6-MPc ($M = 2\text{H}^+$ or Cu^{2+})

The Au₂S Solubility at Elevated Temperatures

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The known thermodynamic instability of Au₂S gold sulfide inhibits its formation in nature and investigation its thermodynamic properties at elevated temperatures as an individual phase. Therefore Au₂S can occur in minerals only as a mineral with low activity (for example, Ag₂S – Au₂S solid solution¹, chemical related forms on surface of sulfides^{2,3}). K(i) of the metastable equilibrium:



has been studied in acid H₂S-containing solutions at 200°C and saturated vapor pressure by precipitation of excessive amounts of the dissolved gold in Au₂S(cr) form immediately under high temperature conditions. The process was conducted in two stages. At the first stage (T=200°C) gold dissolved in autoclaves with the solution of 0.14 m H₂S+0.1 m NaOH by mixing during 14 hours. At the second stage the fixed amount of 2 m HCl has been inserted into the autoclave reheated up to 200°C through the valve with the internal shutoff needle using hydraulic micro press. The solution is additionally acidated up to pH = 1.2 ÷ 1.6 as 0.1 m NaOH is completely neutralized. XRD pattern for deposited phase corresponds to Au₂S (JCPDS card 26-0728). lgK(i) = 2 lgm_{Au(HS)[°]} - lgm_{H₂S(aq)[°]} = -8.3 ± 0.2 has been determined from sulfide sulfur concentrations in H₂S(aq) form and gold in the solution which is referred to Au(HS)[°] complex prevailing in the essentially acid solutions^{4,5} (see Table).

Method	lgK(i)				Reference
	25	100	200	300°C	
Calculation	-14.02	-10.16	-7.63	-6.87	4
Experiment	-13.66 ± 0.03				5
			-8.3±0.2		Our data
Calculation	-15.53	-11.47	-8.65	-7.70	1

Calculations have been conducted: ¹ - by the equation of G[°]_f extrapolation for the reaction of Au₂S(cr) formation from Au(cr) and S₂(gas) at P = 1 bar; ⁴ – using standard thermodynamic properties and heat capacity equation for Au₂S(cr) (P = 1 bar). It is seen that the determined K(i) value is intermediate between its calculated values, which have been obtained with the use of different G[°] data for Au₂S. Taking Au₂S activity to be 0.001 (it is suggested that it exists as a sulfide mineral – see above), according to K(i) constant gold sulfide should be more stable than metal gold at T>100°C. The same situation should occur when Au₂S activity is equal to 0.01 suggesting that temperature rise benefits further increase of the degree of gold concentration in the ‘invisible’ sulfide form.

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Relative Enthalpy and Entropy of Partition Behavior for Pentachloro Biphenyls Observed by Isothermal Gas Chromatography

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For Dioxins and polychlorinated biphenyls (PCBs), which are well known as environmental contaminants, there are many reports on the investigation of their accumulation in the environmental and the biological systems, and the fate of them in the systems has been paid much attention. To estimate the fate, the elucidation of various physicochemical properties such as aqueous solubility, melting points, and partition behavior of them is essential. Especially properties of their chloro-position isomers have been much required, since biological activities among the isomers closely depend on the substituted positions. However, there have been few reports on the properties.

In this study, capillary column retention time of all 46 pentachloro biphenyl isomers (PeCBs) was observed with isothermal gas chromatography (iso-GC). All the samples were prepared by mixing three or four kinds of isooctane solutions of each PeCB. 2,2',4,6,6'-PeCB (No. 104 for IUPAC) was used as the internal standard since the retention time is the shortest in that of all PeCBs. All the iso-GC experiments were performed on GC-14B (SHIMADZU, Kyoto, Japan) equipped with a split capillary injector and a flame ionization detector. The injector and the detector were maintained at 250 °C and 300 °C, respectively. The capillary column utilized for chromatography was 50 m (length) × 0.22 mm (inner diameter) in dimension and was coated with a 0.25 μm-thick film of 8% phenyl polycarborane-siloxane (HT8-PCB, SGE, Melbourne, Australia). The retention time measurements were conducted from 180 °C to 230 °C with a 5 °C temperature interval. From the dependence of the retention time on the column temperature, two thermodynamic parameters of PeCBs, the relative enthalpy, $\Delta(\Delta H)$, and the relative entropy, $\Delta(\Delta S)$, were calculated in term of the van't Hoff relation.

A marked linear relationship between $\Delta(\Delta H)$ and $\Delta(\Delta S)$ was found, but a clear intersection point (compensation temperature) for all 45 PeCBs was not observed in the range of the tested temperature. Therefore, the observed relationship was regarded as a classical enthalpy and entropy compensation.¹ In addition, since both of the $\Delta(\Delta H)$ and the $\Delta(\Delta S)$ depended on the number of chlorine atoms substituted at 2-, 2'-, 6-, and 6'-positions (so called *ortho*-positions), respectively, it seemed that the planarity of biphenyl skeleton was closely related to the thermodynamic properties. From the further analysis on the relationship, it was found that significant difference from the linearity between the $\Delta(\Delta H)$ and the $\Delta(\Delta S)$ was governed by the number of a pair of chlorine atoms substituted at a proximitive position (Npx-Cl). We have already pointed out that the retention times of PCBs depends on not only the chlorine atoms substituted at *ortho*-positions but also them substituted at the proximitive positions.² This dependence implies that Npx-Cl also plays an important role in the partition behavior of chloro-position isomers under the iso-GC measurement.

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Pressure dependence of solubility of α -cyclodextrin in water

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Solubility of several inorganic and organic compounds in water or organic solvents has been measured at high pressure up to 400 MPa in our laboratory using the high-pressure vessels designed by one of us¹. We measured the solubility of α -cyclodextrin (CD) in water up to 50.0 MPa at 298.2 K in this study.

An excess of α -CD and water and a Teflon ball were put into a pressure vessel with an outlet valve. The sample mixture was pressed with a hydraulic pump and the vessel was shaken on a seesaw in a water bath at 298.2 ± 0.1 K for a week. After the equilibration the solution was slowly taken out from the vessel keeping the high pressure. The solution was dried and weighed following ref. [2].

Solubility of α -CD in water at 298.2 K was estimated to be 0.1323 ± 0.0008 mol kg⁻¹ at 0.10 MPa and 0.1476 ± 0.0014 mol kg⁻¹ at 50 MPa. The former coincides with 0.1318 mol kg⁻¹ measured by Jozwiakowski and Connor at the same condition². Pressure coefficient of logarithm of the solubility of α -CD is thermodynamically related to eqs.1-3, where V_c is molar volume of solid α -CD· n H₂O, V_{sat} , partial molar volume of α -CD at saturated concentration, $V_{\text{H}_2\text{O}}$, that of water at saturated concentration, γ , activity coefficient of α -CD, m_s , the solubility of α -CD, and n , the number of molecules of water in the formula of the hydrate ($n = 6$ for α -CD· n H₂O). Using reference data for these parameters the slope can be estimated to be $(\partial \ln m_s / \partial p)_T = (5 \pm 5) \times 10^{-4}$ MPa⁻¹. This positive value thermodynamically supports an enhancement of the solubility by pressure up to 50 MPa.

(1)

(2)

(3)

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Liquid Phase Microextraction and Ultratrace determination of Cadmium by Modified Graphite Furnace Atomic Absorption spectrometry

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A simple and powerful microextraction technique was used for determination of cadmium in water samples using liquid phase microextraction (LPME) followed by graphite furnace atomic absorption spectrometry (GF-AAS). In a preconcentration step, cadmium was extracted from a 2 ml of its aqueous sample in the pH =7 as 5, 7-dibromoquinoline-8-ol (DBQ) complex into a 4 μl drop of benzyl alcohol. After extraction, the micro drop was retracted and directly transferred into a graphite tube modified by [Pd(c)+Pd(i)]. Some effective parameters on extraction and complex formation, such as type and volume of organic solvent, pH, concentration of chelating agent, extraction time and stirring rate were optimized. Under the optimum conditions, the enrichment factor and recovery were 450 and 90%, respectively. The calibration graph was linear in the range of 0.008-1 $\mu\text{g L}^{-1}$ with correlation coefficient of 0.9961 under the optimum conditions of the recommended procedure. The detection limit based on the 3Sb criterion was 0.0035 $\mu\text{g L}^{-1}$ and relative standard deviation for (RSD) for eight replicate measurement of 0.1 $\mu\text{g L}^{-1}$ and 0.4 $\mu\text{g L}^{-1}$ cadmium was 5.2 and 4.5% respectively. The characteristic concentration was 0.0032 $\mu\text{g L}^{-1}$ equivalent to a characteristic mass of 12.8 fg. In order to evaluate the accuracy and recovery of the presented method the procedure was applied to the analysis of reference materials and seawater.

Keywords: Liquid phase microextraction, Preconcentration, Graphite furnace atomic absorption spectrometry, Cadmium, 5, 7-dibromoquinoline-8-ol.

Phosphoramidic Fluoride Complexes with Tin Tetrachloride : A Variable-Temperature NMR study in Solution

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The behaviour of the octahedral complexes $\text{SnCl}_4 \cdot 2(\text{O})\text{P}(\text{NR}_2)_2\text{F}$ (**1**)¹ and $\text{SnCl}_4 \cdot 2(\text{O})\text{P}(\text{NR}_2)\text{F}_2$ (**2**)² (R= Me or Et) has been studied by variable temperature multinuclear (¹H, ³¹P, ¹⁹F and ¹¹⁹Sn) NMR in dichloromethane solutions. The NMR data showed the presence of a mixture of cis and trans isomers for **1** and only the cis isomer for **2**. The latter complex, the cis isomer, more labile and exchanging with free ligand, dissociates measurably in solution. The concentrations of the various species at different temperatures were determined by integration of spectra and the two equilibrium constants K_{iso} for **1** and K_{d} for **2** were calculated. From the temperature variation of the equilibrium constants, the enthalpies and entropies of reaction for the two equilibria were also calculated. The lability of complex **2** may be explained by the unfavourable entropy of reaction. The results are compared with those of the hexamethylphosphoramide complex.³

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SOLUBILITY IN TERNARY SYSTEMS WITH ACETONITRILE

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The data on solubility in ternary systems with acetonitrile (A), submitted in the review ¹ are compared and analyzed. On structure 191 ternary systems are divided into four groups:

[1] A + water (W) + inorganic compound (33 systems or 17 %); [2] A + W + organic compound (43 systems or 23 %) [3] A + inorganic + organic compounds (14 systems or 7 %) and [4] A + two organic compounds (101 systems or 53 %).

Data for ternary systems containing acetonitrile have been measured, published and presented primarily in two forms; either as data at constant temperature or as data collected at polythermal conditions. In the first case (isothermal), the investigator is looking for the composition of a saturated solution at a chosen temperature. Such data have the advantage that results from different studies can often be directly compared. In the second case (polythermal) the investigator prepares a mixture of known composition and then determines the solubility temperature of two or three phases. Such data generally require interpolation between measured data points before comparisons between studies is possible. The majority of the presented ternary systems (173 systems or 91 %) concern to the first case and insignificant part (18 systems or 9 %) - to the second case.

Ternary systems with limited mutual solubility of components representing interest for liquid extraction have been classified by Treybal as: systems with one pair partially miscible liquids (Type I); with two pairs of partially miscible liquids (Type II); with three pairs of partially miscible liquids (Type III) and forming solid phases (Type IV). 92 ternary systems with acetonitrile (or 48 %) are Type I.

Solubility data at several temperatures are described by an algebraic equation. The following equations were utilized most often:

$$y = a + b \cdot x + c \cdot x^2 + d \cdot x + e \cdot x^{3/2} \quad (1)$$

$$y = a + b \cdot x + c \cdot \ln(x) + d \cdot (\ln(x))^2 + e \cdot x \quad (2)$$

These smoothing equations give smaller standard deviations than any other tested equations. The equation parameters were calculated by the least squares method and presented in Tables. The solubilities calculated by the proposed equations are presented in the Figures and Tables.

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Measurements and Predication Range of Solid Compounds in Systems with Ionic Liquid

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In present time there is an increasing focus on ionic liquids. Ionic liquids will probably be used as alternative “greener” solvents instead of volatile organic solvents. Solid-liquid equilibrium has been measured for ternary cuts in two organic systems. Systems were contained of carboxylic acid (acetic acid or propanoic acid) + formamide + ionic liquid 1-butyl-3-methylimidazolium chloride. Solid-liquid equilibrium in the systems was measured from time-temperature warming curves.

In the binary system acetic acid (1) – formamide (2) a stable solid compound was investigated with a formula $(\text{CH}_3\text{COOH})_2\cdot\text{HCONH}_2$. Another stable solid compound, $\text{CH}_3\text{CH}_2\text{COOH}\cdot(\text{HCONH}_2)_2$, was examined in the binary system propanoic acid (1) – formamide (2). In both measured ternary cuts in systems the original solid compounds [1,2] are formed through a strong cross-association O...H...N after an addition of ionic liquid 1-butyl-3-methylimidazolium chloride.

Dissociation thermodynamics quantities were calculated for solid compounds from binary systems.

Obtained estimation of the range of solid compounds was compared with experimental data. This estimation predicts metastable solid compounds in contrast to measured stable solid compounds.

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Solubility determination of Aspirin in Methanol, Ethanol, and Acetone from 298 to 323 K

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Aspirin, or acetylsalicylic acid is a salicylate. The behavior of the acetylsalicylic acid solubility in different temperatures affects, among other aspects, the choice of a crystallization, purification, and storage process. A series of solubility values for acetylsalicylic acid in certain solvents under a given temperature as well as physical and chemical properties of acetylsalicylic acid¹⁻⁴. This study is aimed at contributing toward the determination of the solubility of acetylsalicylic acid in three solvents, i.e., methanol, ethanol, and acetone in different temperatures. In this work, the solubility of acetylsalicylic acid in three organic solvents, methanol, ethanol, and acetone were measured by a gravimetric method from (298 to 323) K and the solubility data was correlated against temperature. The solubility of acetylsalicylic acid in acetone was high compared with other solvents. Within the temperature range of the measurements, solubility of acetylsalicylic acid in the solvents increased with an increase in temperature. drug, often used as an analgesic to relieve minor aches and pains, as an antipyretic to reduce fever, and as an anti-inflammatory medication. It also has an antiplatelet or "anti-clotting" effect and is used in long-term, low doses to prevent heart attacks, strokes and blood clot formation in people at high risk for developing blood clots.

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Solubility Determination of Caffeine in Several Organic Solvents at Different Temperatures

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Caffeine ($C_8H_{10}O_2$) is an alkaloid whose basic structure is purine, and available in tea, coffee, cola nut and cacao. Caffeine is extensively used in non-alcoholic beverages and also in pharmaceuticals because of its stimulant and muscle relaxant properties. The most dominant alkaloid in the purine compounds is caffeine¹. Generally, caffeine is extracted from plants such as cacao, tea and coffee. These methods are based on extraction from the filtrates of water-plant systems by means of solvents. The extraction processes depend upon the plants and solvents selected. Solvent extraction processes can be divided into two broad categories according to the origins of the differential **solubility**. On the one hand, it arises from purely physical differences between the two solutes, such as polarity, while in other cases it can be traced to definite chemical interaction between solute and solvent²⁻⁵. Caffeine extraction is an important industrial process and can be performed using a number of different solvents. In this work, the solubility of caffeine in seven organic solvents, ethyl acetate, ethanol, methanol, carbon tetrachloride, chloroform, dichloromethane, and acetone were measured by a gravimetric method from (298 to 348) K and the solubility data was correlated against temperature. The solubility of caffeine in chloroform and dichloromethane was high compared with other solvents. Within the temperature range of the measurements, solubility of caffeine in the solvents increased with an increase in temperature. The solubility of caffeine decreases in the order of chloroform, dichloromethane, acetone, methanol, ethyl acetate, ethanol and carbon tetrachloride.

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Solubility of Rutin in Methanol, Ethanol, Ethyl Acetate and Acetone in Different Temperatures

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Rutin a naturally occurring polyphenolic compound which is present in different fruits, vegetables, and seeds has many biological and pharmacological activities including antioxidative and, anti-inflammatory and, and antitumor effects. In this study, the solubilities of rutin in water, methanol, ethanol, acetone, and ethyl acetate were determined at different temperatures by a gravimetric method. The experimental data of solubilities were correlated using a simplified thermodynamic equation and an empirical equation. The solubilities of rutin in different solvents, which are usually used in laboratory and related industries, were measured by using a saturation method. The solubilities of rutin in pure solvents in this work increase with rising temperature.

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Effects of pressure and temperature on the solubility of naphthalene in water

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Solubility of naphthalene in water was measured at 273.2 - 313.2 K and 0.1 - 200 MPa. Logarithm of the solubility was linearly decreased with increasing pressure at each pressure. Volume changes for the dissolution, ΔV , were estimated to be 11.2, 12.1, 14.5 and 17.5 cm³mol⁻¹ at 273.2, 283.2, 298.2 and 313.2 K, respectively, using $\Delta V = -RT [\partial(\text{solubility}) / \partial p]_T$. The ΔV corresponds to the volume difference between the partial molar volume in water, V^∞ , and molar volume, V_s , of solid naphthalene; $\Delta V = V^\infty - V_s$. Because the ΔV does not depend on pressure and the V_s should decrease with increasing pressure, V^∞ should decrease with increasing pressure without any maximum. On the other hand, V^∞ of alkylbenzenes (toluene, ethylbenzene, and *n*-propylbenzene) have shown a maximum around 100 – 200 MPa¹ and the compressibility ($-\partial V^\infty / \partial p$)_T of V^∞ of methylene group (-CH₂-) in water is well known to be negative at 0.10 MPa². It may be ascribed to any difference in hydration structure between naphthalene and alkylbenzene.

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Na₂CO₃ Solubility Behavior in Ternary Hydrothermal Systems with Various Salts of Type 1.

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POSTER PRESENTATION

Solubility of sodium carbonate (Na₂CO₃) in water sharply decreases with temperature increase approaching to the critical temperature of pure water. Binary system Na₂CO₃ - H₂O belongs to type **2** systems with the critical end-points in solid saturated solutions (point **p** (l=g-s) ~ 374 °C, and point **Q** (l₁=l₂-s) ~ 480 °C) and the supercritical fluid region, where a homogeneous fluid (saturated with solid phase or not) does not separate into two solutions at any variation of pressure.

An influence of the second salt addition on phase behavior of Na₂CO₃ - H₂O mixtures was studied under supercritical conditions. As the second salt was used NaCl, K₂CO₃ or Na₂WO₄, which belongs to type **1** and forms with water the binary system characterized by a high salt solubilities in water at near-critical temperatures and by an absence of both the critical phenomena in solid saturated solutions and the supercritical fluid region. However, the hydrothermal solutions of K₂CO₃ and Na₂WO₄ are characterized by liquid-liquid immiscibility, whereas the immiscibility phenomena are absent in aqueous NaCl solutions.

It was established that solubility of Na₂CO₃ at 425-475 °C in three-phase equilibrium (g(l₁)-l₂-s_{Na₂CO₃}) of ternary systems with K₂CO₃ and Na₂WO₄ is higher than in the ternary system Na₂CO₃ - NaCl - H₂O under the same conditions. It is shown also that the pressures of 3-phase equilibrium in the systems Na₂CO₃ - Na₂WO₄ - H₂O and Na₂CO₃ - K₂CO₃ - H₂O are higher than that in Na₂CO₃ - NaCl - H₂O system at the same temperatures and contents of type **1** salts. Critical pressures in solid saturation solutions with K₂CO₃ and Na₂WO₄ are higher than the critical pressures in the system with NaCl at the same temperatures. Another special feature is a behavior of monovariant critical phenomena in a vicinity of the second critical endpoint **Q**.

An explanation of such different behavior of salt solubility and critical phenomena is connected with a different nature of phase equilibria in the binary subsystems of type **1**. As a result an addition of type **1** salt to supercritical fluid, spreading from the binary subsystem Na₂CO₃ - H₂O, leads to a separation of homogeneous fluid into two liquids along the monovariant critical curve l₁=l₂-s_{Na₂CO₃} in the case of K₂CO₃ and Na₂WO₄. However, the same fluid transforms into liquid and gas along the monovariant critical curve l=g-s_{Na₂CO₃} if NaCl is added.

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The study of kinetic and thermodynamic oxidation of Ponceau S by $K_2S_2O_8$ with $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_2$ and $Fe(NO_3)_3$ catalyst

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The reactions were followed by the spectrophotometric method at a wavelength of 520nm. and the influence of the effective factors such as reactions temperature, viscosity of the reactants, type of catalyst and solution on the rate of P.S absorption were studied. The variation n of the reaction rate with temperature was measured and the thermodynamic quantities such as Enthalpy, Entropy, and Gibbs free energy as well as the order of the reactions, the rate constants and Arrhenius parameters were determined.

Pressure dependence of solubility of α -cyclodextrin in water

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Solubility of several inorganic and organic compounds in water or organic solvents has been measured at high pressure up to 400 MPa in our laboratory using the high-pressure vessels designed by one of us¹. We measured the solubility of α -cyclodextrin (CD) in water up to 50.0 MPa at 298.2 K in this study.

An excess of α -CD and water and a Teflon ball were put into a pressure vessel with an outlet valve. The sample mixture was pressed with a hydraulic pump and the vessel was shaken on a seesaw in a water bath at 298.2 ± 0.1 K for a week. After the equilibration the solution was slowly taken out from the vessel keeping the high pressure. The solution was dried and weighed following ref. [2].

Solubility of α -CD in water at 298.2 K was estimated to be 0.1323 ± 0.0008 mol kg⁻¹ at 0.10 MPa and 0.1476 ± 0.0014 mol kg⁻¹ at 50 MPa. The former coincides with 0.1318 mol kg⁻¹ measured by Jozwiakowski and Connor at the same condition². Pressure coefficient of logarithm of the solubility of α -CD is thermodynamically related to eqs.1-3, where V_c is molar volume of solid α -CD· n H₂O, V_{sat} , partial molar volume of α -CD at saturated concentration, $V_{\text{H}_2\text{O}}$, that of water at saturated concentration, γ , activity coefficient of α -CD, m_s , the solubility of α -CD, and n , the number of molecules of water in the formula of the hydrate ($n = 6$ for α -CD· n H₂O). Using reference data for these parameters the slope can be estimated to be $(\partial \ln m_s / \partial p)_T = (5 \pm 5) \times 10^{-4}$ MPa⁻¹. This positive value thermodynamically supports an enhancement of the solubility by pressure up to 50 MPa.

(1)

(2)

(3)

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