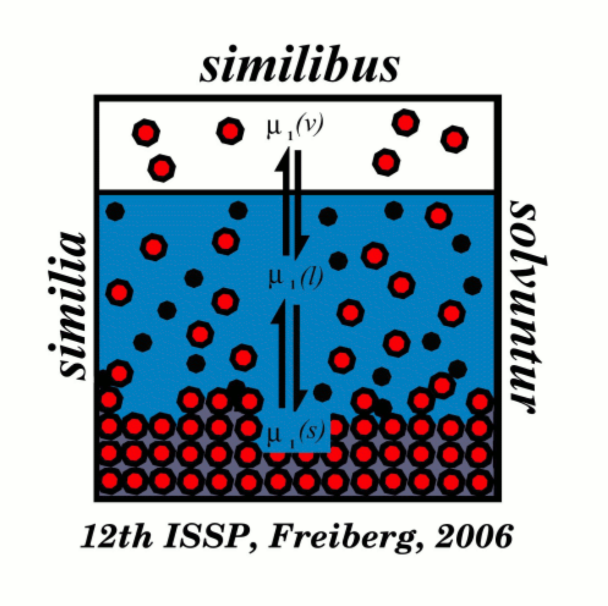
# 12th International Symposium on Solubility Phenomena and Related Equilibrium Processes

# ISSP 2006



TU Bergakademie Freiberg, Germany

July 23th-28th, 2006

# Abstract Volume

# Preface

Solubility represents the central term and topic of the ISSP conference series, which is organized by the IUPAC Subcommittee on Solubility and Equilibrium Data in even numbered years at different places in the world:

| | | |
|---|---|---|
| **1984** | **1st** | **ISSP, London, ON Canada, The University of Western Ontario** |
| **1986** | **2nd** | **ISSP, Newark, NJ, New Jersey, Institute of Technology** |
| **1988** | **3rd** | **ISSP, Guildford, Surrey, UK, University of Surrey** |
| **1990** | **4th** | **ISSP Troy, NY, USA, Rensselaer Polytechnic Institute** |
| **1992** | **5th** | **ISSP Moscow, Russia, Russian Academy of Sciences** |
| **1994** | **6th** | **ISSP Buenos Aires, Argentina** |
| **1996** | **7th** | **ISSP Leoben, Austria, Montanuniversität Leoben** |
| **1998** | **8th** | **ISSP Niigata, Japan** |
| **2000** | **9th** | **ISSP Hammamet, Tunisia** |
| **2002** | **10th** | **ISSP Varna, Bulgaria** |
| **2004** | **11th** | **ISSP Aveiro, Portugal** |
| **2006** | **12th** | **ISSP Freiberg, TU Bergakademie Freiberg** |

Industrial and cultural development of Freiberg, the conference place of this year is closely related to solubility phenomena, which had formed the rich deposits of metal ores and silver in the region of “Erzgebirge” (“ore mountains”) – the basis for prosperity of the city over hundreds of years. The roots of modern geological and metallurgical sciences trace back to the foundation of the university “Bergakademie Freiberg” 240 years ago. From the beginning the university attracted always scientists and students from all over the world. Therefore, we are proud to welcome scientists from 30 countries at the university campus. The scientific programme reflects to a certain extent the geological, mineralogical and environmental background. However, solubility phenomena are discussed in a broad scope from gas solubility to gas hydrate formation, systems under conditions of high pressure and temperature, thermodynamic modelling and crystallization. At this conference we continued with organizing a workshop on a special topic related to solubility, as it was initiated at the 10th ISSP in Varna. This time “quality assurance of thermodynamic databases” will be discussed. The organizers wish all participants a pleasant stay in Freiberg and fruitful exchange of scientific ideas and experience.

Organizing Committee
Freiberg, July 2006

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# PLENARY LECTURE

## GAS SOLUBILITY IN AQUEOUS AND NON-AQUEOUS SOLUTIONS

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The solubility of gases in water as well as in aqueous and non-aqueous solutions has been the topic of many publications. Nevertheless, there is still a strong interest in gas solubility due to its importance in many areas, e. g., in chemical engineering, environmental protection etc. and also due to new solvent systems (e. g. ionic liquids) which have recently found a lot of attention. This contribution is to present some typical examples for experimental and theoretical work in the area of gas solubility in pure solvents as well as in solvent mixtures. The examples deal with "physical" as well as with "chemical" gas solubility. However, also the limits of that commonly used classification will be shown.

Experimental results will be presented to discuss the typical phenomena. Examples will be given also for the correlation/prediction of the solubility of gases. Classical thermodynamics (i. e. combining Henry's law constant with expressions for the Gibbs excess energy of the liquid mixture), as well as molecular simulation results will be presented to demonstrate the currently available methods for calculation and predicting the solubility of gases in "complex" systems. The examples include

- the solubility of a single gas (e.g., ammonia and carbon dioxide) in water and in aqueous solutions of strong electrolytes ("salting-out" and "salting-in" phenomena)
- the solubility of a single gas in an aqueous/organic solvent mixture
- the simultaneous solubility of ammonia and carbon dioxide in water and in aqueous solutions of a strong electrolyte
- the solubility of a sour gas in aqueous solutions of an amine
- the solubility of an inert gas in an ionic liquid.

# SHORT COMMUNICATION

## CARBON DIOXIDE SYSTEMS IN AQUEOUS PROCESSES

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Carbon dioxide as a useful reactive ingredient has increasingly gained interest in several process industries. These include buffered carbonate- and alkaline systems that depend on the solubility and reactivity of the reactants. $CO_2$ gas is commonly used for pH control that facilitates dissolution and precipitation of carbonates. Techniques for removing acid gases from flue gases by absorption are commonly used in coal gasification and sweetening of natural gases. In these systems aqueous alkanolamine mixtures have traditionally been used. Recently ionic liquids have been studied for $CO_2$ absorption and other industrial applications.

For process design, we require knowledge of molecular interactions, speciation and solubilities as well as chemical equilibria in reactive multiphase systems. At specified temperature and liquid composition, the total pressure of the system is mainly determined by the non-dissociated molality (or molefraction) of dissolved $CO_2(aq)$ according to Henry's law. The non-dissociated $CO_2(aq)$ is in equilibrium with ionic bicarbonate, carbonate and other ionic species in the system, and with solid phases. Modeling of both phase equilibia and chemical equilibria provides a rigorous tool for describing aqueous industrial and environmental processes that include chemical reactions, sources and sinks of $CO_2$.

For process optimization, chemical equilibrium data are increasingly needed to interpret complex industrial and natural systems that contain aqueous electrolytes and precipitates. Thermodynamic analysis provides quantitative relations among chemical energy, chemical reactions, solubilities of gases and salts, and important online process parameters like pH, temperature and pressure. Supported by laboratory experiments, and by pilot- and mill-scale experience, models have provided applications in different industries where $CO_2$ is a reactant. For example, in the pulp and paper industry the properties of wood fibre combined with the results of model calculations can be used to reduce heating and raw-materials cost. New industrial applications include cleaning waste- and process waters as well as recovering valuable or environmentally harmful metal ions as carbonates. The current trend toward using carbon dioxide is partly due to increased demand for making chemical processes environmentally friendlier. Carbon dioxide can replace more harmful chemicals. Sometimes the $CO_2$ process is better as it replaces more harmful chemicals or it is economically superior.

Best available techniques and continuous improvements are needed to produce an environmentally acceptable, energy-efficient process with ever-smaller input of chemicals, raw materials, and water.

# SHORT COMMUNICATION

## A NEW SIMPLE METHOD FOR THE INVESTIGATION OF HYDROGEN SULPHIDE SOLUBILITIES IN AQUEOUS SOLUTIONS

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Compared to other natural gases only few investigations of hydrogen sulphide ($H_2S$) solubility in aqueous solutions of inorganic salts were conducted [1]. This may be attributed to the uncomfortable nature of this compound (odour, toxicity) and the complexity of experimental designs proposed so far (e.g. [2], [3]). Most of them include open flow-through systems: the gas is bubbled through the solution until equilibrium is assumed or proved by stepwise analysis of the fluid phase.

We have developed a closed system approach, where the only analytical quantity is the total gas pressure. The apparatus consists of a three-necked flask with a continuously measuring datalogging pressure sensor on top of one neck and two septa on the others (WTW Oxitop® system). First the flask is filled with a pure $H_2S$ atmosphere of unit pressure and thermostated at 25°C ± 1°C. Then a certain volume of deaerated salt solution is injected through one septum. The process of equilibration is continuously controlled by the pressure sensor, the recorded data of whom are read out via an infrared device.

Equilibrium is attained within about an hour of magnetic strirring. At constant temperature the aqueous hydrogen sulphide concentration may be derived easily from known or measured quantities like the final gas pressure, the flask volume and the solution volume. The apparatus once filled with $H_2S$ and an initial solution may be used for several consecutive measurements simply by injecting additional quantitites of water (fig. 1). We applied this new technique to investigate $H_2S$ solubilities in concentrated solutions of NaCl, KCl, $MgCl_2$, $Na_2SO_4$, $K_2SO_4$ and $MgSO_4$.

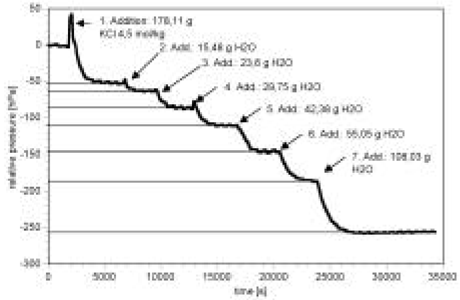

Fig. 1: $H_2S$ pressure above KCl

**Acknowledgements**
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# SHORT COMMUNICATION

## DIELECTRIC PROPERTIES, WATER ACTIVITY OF ELECTROLYTE SOLUTIONS AND PHASE DIAGRAMS WATER-SALT SYSTEMS.

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The static dielectric constant ($\varepsilon_s$) directly reflects the hydration characteristics in comparison with other thermodynamic characteristics of solutions. The method of dielectric microwave spectroscopy (7-25 GHz) is advanced for the analysis the dielectric and relaxation parameters of the salt saturated solutions. The experimental values of $\varepsilon_s$ for 15 binary and 10 ternary water-salt systems (including the saturated solutions) were obtained. Correlation between the changes $\varepsilon_s$ and relaxation parameters (that reflect the molecular-kinetic state of water in solutions through time and enthalpy of the dielectric relaxation) is considered. It is experimentally revealed: 1) Significant difference of $\varepsilon_s$ values in different concentration structural areas (in concentrated solutions $\varepsilon_s \sim 20\text{-}40$); 2) The opposite sign of the temperature changes of $\varepsilon_s$ for high concentrated solutions of binary and ternary systems; 3) The unusual order of $\varepsilon_s$ changes with the change of ionic charge and radius that connect with the presence of ion-ion interactions; 4) Correlation of $\varepsilon_s$ changes with complexation (on the data of electronic spectra Cu (II)); 5) The absence of additivity of $\varepsilon_s$ changes at transition from binary to multicomponent systems in the case of the saturated solutions, where the ion-ion groups are present.

The values of $\varepsilon_s$ practically do not vary in concentration areas where the crystallization of double salts is observed. It is caused by formation of complex ionic groups in solutions of above-mention concentration areas. “Special points” of solubility diagrams are displayed on the properties of solutions.

The thermodynamic properties of concentrated saturated solutions were analyzed on the basis of semi-empirical Debye’s and Pitzer’s equations. These methods of description were shown to be “effective” at the molecular level if dielectric constants of concentrated solutions are unknown or impossible to be included.

The real experimental values of $\varepsilon_s$ solution usually were not used for activity coefficient calculations in above-mentioned equations. We analyzed influence of $\varepsilon_s$ on the results of calculations for the phase diagram and activity coefficient. The connection of the osmotic coefficient, the water activity, the static dielectric constant and the structural variations of concentrated and saturated solutions were considered. It was established the linear correlation of the water activity with the dielectric constant inverted value for electrolyte solutions up to the high concentration (4-5m).

The osmotic and activity parameters of saturated solutions and phase equilibria in ternary and quarternary systems (among them Ba, Y, Cu-nitrates) were calculated on the basis of Pitzer’s equations, own experimental and literary data on the water activity in binary or ternary systems. The method for calculation of thermodynamic properties of saturated solutions and phase equilibria in multicomponent systems was developed using this approach. It includes the calculations of parameters for multicomponent systems, the solubility of compounds and the experimental testing of the calculated solubility data in special points of phase diagrams.

*This work was supported by the grants of Presidium RAS and RFBR ? 05-03-32100.*

# SHORT COMMUNICATION

## SOLUBILITY OF IONIC LIQUIDS AND THEIR USE AS SOLVENTS IN SEPARATING ORGANIC LIQUIDS

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Ionic Liquids offer a new and exciting range of solvents for both extractive distillation and solvent extraction processes for separating organic liquid mixtures. In this work the SOLUBILITY of ionic liquids is the focus of an investigation into the separation of organic liquid mixtures such as aromatic compounds from aliphatic compounds. The ionic liquids include: $[HMIM]^+ BF_4^-$ , $[HMIM]^+ PF_6^-$ , $[BMIM]^+ PF_6^-$ , $[OMIM]^+ Cl^-$ , $[BMPY]^+ BF_4^-$ , $[EMIM]^+ I_3^-$, $[BMIM]^+ I_3^-$ , $[EMIM]^+ C_8H_{17}SO_4^-$, $[BMIM]^+ CH_3(OC_2H_4)_2SO_4^-$ and phosphonium ionic liquids - trihexyl-tetradecyl phosphonium chloride or tris(pentafluoroethyl)trifluorophosphate.

The tie-lines of ternary phase diagrams are used to determine the selectivity of each ionic liquid for a particular separation process and the efficacy of each ionic liquid is then predicted. Although these selectivity values are important they must be looked at with other phase diagram properties in mind, such as the magnitude of the partially miscible region and their solubility, when considering commercial separation.

The ternary phase diagrams are dependent on the mutual solubilities of the three components involved. These solubilities can be used to predict crude phase diagrams and tie-line data for any ionic liquid + organic liquid mixtures.

The phase equilibria and solubility data, discussed in this work, have been obtained in the author's laboratory and from data reported in the literature. The results in this work have also been extrapolated to predict the molecular structures of potentially more effective ionic liquids for the separation processes discussed here. These selectivities also have a bearing on the efficacy of ionic liquids in separating liquids using extractive distillation.

Activity coefficients at infinite dilution of organic liquid solutes in Ionic Liquid solvents have also been measured in order to predict the possibility of using these Ionic Liquids as solvents in extractive distillation processes. The results of our work and those of other workers are discussed in this work and related to the conclusions obtained from the phase equilibria work. The importance of the solubility of the ionic liquids is stressed in this work.

# INVITED LECTURE

## LI-AIR BATTERIES: A CLASSIC EXAMPLE OF LIMITATIONS DUE TO SOLUBILITIES

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The applications for high energy, high capacity batteries are rapidly expanding having enormous impact on various advances in mobile electronic equipment for both commercial and military applications. Metal-air batteries (e.g. Zn-air, Al-air) which are aqueous systems have been studied for many years since their specific capacities (mAh/g) are much higher than conventional batteries such as NiCad, Ni-metal hydride, Li and Li-ion. The reason for these high specific capacities is that the cathodic reactant, $O_2$ from air, does not have to be stored under high pressure in steel vessels which would significantly increase the total mass of the battery. However, the aqueous Zn and Al metal air batteries systems exhibit low operating voltages of around 1.2 to 1.3 V which results in low practical specific energies (Wh/kg). Replacing Zn or Al anodes with Li offers significant advantages due to the high potential of Li anodes and its low molecular mass. In developing Li-air cells and batteries (commonly referred to as a Li-air *semi-fuel cell*), a number of obvious limitations have to be addressed, a major one being the prevention of ingress of water from the atmosphere via the fuel cell air electrode into the electrolyte solution resulting in reaction with metallic lithium posing a serious safety problem.

Li-air semi-fuel cells are basically composed of a metallic Li anode and an air ($O_2$) fuel cell cathode. The air electrode serves to provide an interface where $O_2$ from air is dissolved in an electrolyte solution and electrochemically reduced at the cathode. Two limitations of the rate capability of the Li-air cell involve $O_2$ solubility and diffusion in the catholyte electrolyte solution. In addition, Li-air cells generally employ a Li-stable, aprotic organic electrolyte solution in which the solubility of water from the atmosphere is low, but not negligible. In aprotic organic-based electrolyte solutions, the products of the cell reactions are insoluble $Li_2O$ and $Li_2O_2$, and the overall (mixed) cell reactions are:

Mechanism 1: $\mathbf{2Li + ½O_2}$ ® $\mathbf{Li_2O}$
Mechanism 2: $\mathbf{2Li + O_2}$ ® $\mathbf{Li_2O_2}$

Both $Li_2O$ and $Li_2O_2$ precipitate in the porous carbon-based fuel cell air electrode which blocks further $O_2$ diffusion into the cathode and thus abruptly ends cell life. To increase the practical deliverable energy and capacity of the Li-air cell, it is advantageous to avoid precipitation of $Li_2O$ and $Li_2O_2$, and this can be accomplished by replacing the aprotic organic electrolyte solution with an aqueous acidic solution. The overall reaction for the aqueous acidic Li-air cell is

Mechanism 3. $\mathbf{2Li + ½O_2 + 2H^+}$ **?** $\mathbf{2Li^+ + H_2O}$

where the reaction products ($Li^+$ and $H_2O$) are soluble in aqueous solutions thereby avoiding precipitation of a lithium oxide, lithium sulfate if the acid is $H_2SO_4$, or lithium chloride if the acid is HCl. A comparison of theoretical open circuit voltages, specific energies and specific capacities for various metal-air cells is given in the Table below (the molecular mass of $O_2$ is not included in these values since $O_2$ is not stored in the working battery).

| Metal-Air System | OCV (V) | Specific Energy (Wh/kg) | Specific Capacity (mAh/g) |
|---|---|---|---|
| $2Li + ½O_2 \rightarrow Li_2O$ (in aprotic organic sln) | 2.913 | 11,248 | 3,862 |
| $Li + ½O_2 \rightarrow ½Li_2O_2$ (organic) | 2.959 | 11,425 | 3,862 |
| $Al + 0.75O_2 + 1.5H_2O \rightarrow Al(OH)_3$ (aq) | 2.701 | 4,021 | 1489 |
| $Zn + ½O_2 \rightarrow ZnO$ (aqueous) | 1.650 | 1,353 | 820 |
| $2Li + ½O_2 + 2H^+$ ? $2Li^+ + H_2O$ (aq) | 4.274 | 14,411 | 3372 |

In order to develop a practical Li-air cell using an aqueous acidic electrolyte solution, it is of course necessary to avoid direct contact of Li with the aqueous solution. This has been achieved by use of a thin (e.g. 75 $\mu$m) proprietary solid-state $Li^+$-conducting glass ceramic membrane to protect the metallic Li anode. Details on these concepts will be presented in the full paper.

# PLENARY LECTURE

## GAS SOLUBILITY IN HYDRATE FORMATION AND DISSOCIATION

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Natural gas hydrates are inclusion solids which have formation and dissociation phenomena directly related to the solubility of gases in the associated liquid water phase. The hydrate compounds are modeled by a solid solution theory which is one of the primary victories of statistical mechanics in everyday industrial usage.

This presentation will review solubility phenomena related to hydrates, and it will show measurements techniques which quantify hydrate solids on a molecular scale. After a brief introduction, and review of fundamental measurements, an overview will be presented of applications in flow assurance, energy resources, seafloor stability, and climate change. Much of the material presented will be a pre-publication of the third edition of the author's first book on the topic, slated for publication in 2007[1].

Perhaps of particular interest to the solubility community, the following questions will be addressed regarding hydrates:

<u>On the Fundamental Side:</u>

1. How can the solid solution swelling model can be inserted into the statistical mechanics model for the most accurate predictions ?
2. How does hydrophobic phenomena, solubility theory and simulation relate to nucleation ?
3. After the thermodynamic challenge is resolved, how can solubility play a role in hydrate kinetic phenomena ?

<u>On the Applied Side:</u>

1. How does solubility of hydrates relate to phenomena of dissolution – in particular to seafloor sequestration of carbon dioxide as hydrates?
2. Is it possible to relate hydrate growth from a supersaturated liquid solution to single phase metastable predictions ?
3. How do solubility, mass transfer, heat transfer, and hydrate kinetics impact hydrate formation and dissociation?

### References

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# SHORT COMMUNICATION

## LIQUID-LIQUID EQUILIBRIA OF TERNARY MIXTURES CONTAINING HFEs AND ALKANES

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Traditional fluorochemicals (CFCs and PFCs) have an unfriendly environmental profile. Because of that, hydrofluoroethers (HFEs) have been recently been proposed as their substitutes. They are used, for instance, in semiconductor industry, as aqueous cleaning medium or also as coolant fluids [1-3]. The HFEs offer useful safety and performance properties similar to CFCs, but offer a more friendly environmental profile because they have a zero ozone depletion potential (ODP) and lower global warming potential (GWP) indices and a short periods of degradation in the atmosphere [4-5]. Moreover, the physical properties of these materials, like low $H_2O$ solubility and high vapour pressure, suggest a low level of risk to aquatic systems [6]. Among HFEs, those which contain an aliphatic chain separated from a perflourated chain stand out, but scarce information of their thermophysical properties (pure component and mixtures) and their phase behaviour are available in literature, and this makes their thermodynamic behaviour description difficult.

In this sense, we present in this work the liquid-liquid equilibria temperature dependence of the mixtures HFE-7100 + n-decane + n-dodecane and HFE-7500 + n-decane + n-dodecane. The liquid-liquid data have been measured at 278.15 K, 288.15 K, and 298.15 K. Phase compositions were measured by gas chromatography from samples splitted isothermally into a glass stirred device. The tie-lines data were correlated using the NRTL [7] and UNIQUAC [8] equations, being gathered the corresponding fitting parameters. UNIFAC group contribution method [9] was applied to predict the inmiscibility region and only a qualitative description was obtained. This effect reveals the importance of a wider disposable of thermodinamic liquid split data for an adequate description of multicomponent heterogeneous systems using group contribution methods.

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# SHORT COMMUNICATION

## LIQUID-LIQUID EQUILIBRIUM OF AQUEOUS SOLUTIONS OF FLUORINATED HYDROCARBONS IN ALCOHOLS AT T = 288.2, 298.2, 308.2 K and p = 101 kPa

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Liquid-liquid equilibrium (LLE) and solubilities of solutions of (fluorobenzene + water + alcohol) and (trifluorotoluene + water + alcohol); alcohol = methanol, or ethanol, or 2-propanol, were established in thermostated cells at T = 288.2, 298.2, and 308.2 K and atmospheric pressure. The titration method was used to construct the binodal curves. Gas-liquid chromatography (Perkin Elmer, Model: Clarus 500) was used to determine the ternary compositions of the mutual phases. The measured LLE data were reduced and correlated by the Othmer, NRTL and UNIQUAC models. The correlated binodal and LLE phase diagrams were in good accordance with experimental data.

The distribution coefficients and separation factors are reported together with the distribution coefficient at infinite dilution for a given solute-solvent pair.
The temperature-dependence of solubility and the component-chemical effect on distribution coefficients is discussed.

The knowledge of LLE data the investigated systems is important for selection of the best solvents in liquid-extraction processes.

# SHORT COMMUNICATION

## ARE SOLUBILITY PARAMETERS RELEVANT TO SUPERCRITICAL FLUIDS?

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Solubility parameters ($d$) are helpful for the indication of the solubility of solutes in liquid solvents. A rule of thumb says that when $d_2$ of a solute is within 4 MPa$^{1/2}$ of that of the solvent $d_1$ the solute should be fairly soluble in it. This rule is applicable to gaseous, liquid, crystalline, and polymeric solutes. The solubility parameters $d_2$ of solutes are available in several compilations and can be estimated from group contributions [1]. Values of $d_1$/MPa$^{1/2}$ of liquid solvents at ambient conditions range from ca. 12 for perfluoro-*c*-hexane to ca. 48 for water. For solute/solvent systems with small mole fraction solubilities: $\ln x_2 = -V_1(RT)^{-1}(d_2 - d_1)^2$, where $V_1$ is the molar volume of the solvent and $R$ and $T$ have their usual meaning.

The solubility products $d_1$ of supercritical fluid solvents have not been studied extensively. Expressions are now presented [2], based on equations of state, for the estimation of the solubility parameters of supercritical fluids. These expressions depend on the critical pressure $P_c$ and the reduced temperature $T_r = T/T_c$ and density $?_r = ?/?_c$ of the fluids as well as their acentric factors $?$ if not conformal with Lennard-Jones fluids:

$$d/\text{MPa}^{1/2} = 3.0(P_c/\text{MPa})^{1/2}T_r^{1/4}?_r[1 + m(1 - T_r)^2]$$

where $m = 0.480 + 1.574? - 0.176?^2$. For those that are conformal an alternative expression depending on the Lennard-Jones parameters $e/k_B$ and $s$ is presented:

$$d/\text{MPa}^{1/2} = 0.1786\,(e/k_B)^{3/4}\,(s/\text{nm})^{3/2}\,T^{-1/4}\,V_1^{-1}$$

A correlation of solubility parameters of room temperature solvents with the Kamlet-Abboud-Taft $p^*$ solvatochromic dipolarity/polarizability parameters is extended to cover also supercritical fluids [2].

The solubility parameters of supercritical fluids can be compared only for corresponding states. At the reduced density $?_r = 1.0$ and the reduced temperature $T_r = 1.2$ the $d$/PMa$^{1/2}$ values of supercritical fluids range from 5.1 for hexane via 8.1 for carbon dioxide to 13.7 for water. In order to dissolve common non-polar solutes the value for supercritical carbon dioxide, the most widely used supercritical fluid, may be adequate or need augmentation by increasing the pressure (and density) and using as low a temperature as feasible. For dissolving polar solutes the use of a polar modifier, such as methanol, is required.

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# PLENARY LECTURE

## THE USE OF SOLUBILITY DATA IN RADIOACTIVE WASTE DISPOSAL

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Radioactive waste arises mainly from the generation of nuclear power but also from the use of radioactive materials in medicine, industry and research. It occurs in a variety of forms with very different physical and chemical properties and may range from slightly to highly radioactive. It is a worldwide consensus that radioactive waste should be disposed of in a permanent way which ensures the protection of humans and the environment. This objective may be achieved by isolating radioactive waste in a disposal system which is located, designed, constructed, operated and closed such that any potential hazard to human health is kept acceptably low, now and in the future.

For highly radioactive waste and spent nuclear fuel, which are the waste types representing the highest potential danger to human health, an effective isolation from the biosphere is considered to be achievable by deep geological disposal. Disposal concepts rely on the passive safety functions of a series of engineered and natural barriers. The performance of these barriers is demonstrated in a comprehensive safety analysis.

Total isolation of the radioactive waste over extended timescales is not possible, and radionuclides will eventually be released from the waste matrix and migrate through the engineered barriers and the geosphere. The assessment of their mobilities in these environments is essential for the safety demonstration of such a repository. The solubility of many radionuclides is limited and may contribute significantly to retention. Reliable predictions of solubility limitations is therefore of key importance.

Predictions of maximum solubilities are always subject to uncertainties. Complete sets of thermodynamic and equilibrium data are required for a reliable assessment of the chemical behaviour of the radionuclides. Gaps in the thermodynamic databases may lead to erroneous predictions. The identification of the solubility limiting solid phase is often difficult. Missing data and insufficient knowledge of the solubility limiting processes increase the uncertainties and require pessimistic assumptions in the safety analysis with respect to the mobility of the radionuclides.

# SHORT COMMUNICATION

## MIXED CRYSTALS FORMATION FROM AQUEOUS SOLUTIONS – A SURVEY

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The mixed crystals are non-stoichiometric compounds in which part of the ions, atoms or molecules constituting the crystal lattice of a given substance have been replaced by the corresponding ions, atoms or molecules of another substance. The extent of mixing depends on the ability of the admixtures to adopt the coordination environment of the substituted particles of the main component. A qualitative measure of this ability is the distribution coefficient, defined as the ratio of the concentrations of the components in the mixed crystal to the ratio of their concentrations in the medium from which the mixed crystal has been obtained under equilibrium conditions. Consequently, the distribution coefficient is a basic thermodynamic characteristic of mixed crystals formation.

Assuming that the admixture component as a pure substance is from the same chemical type as the main component and possesses an isodimorphic structure which is isostructural e.g. isomorphic with the crystal structure of the main component, the distribution coefficient will be given by

$$D = A.\exp(-?\,G_{I\rightarrow II})/RT$$

where $?\,G_{I\rightarrow II}$ is the free energy of the phase transition between the two isodimorphic structures e.g. between the crystal structure of the main component and the crystal structure of the admixture as a pure substance. In the particular case when the crystal structures of the main component and the admixture are isomorphic, i.e. $?\,G_{I\rightarrow II}$ ˜ 0, the distribution coefficient will be determined by the preexponential factor alone. In cases when mixed crystals of salts of the same chemical type are formed in solutions, this factor will be given by the equation:

$$A = (M_1.?_1.?_2.f_1)/(M_2.?_2.?_1.f_2).$$

Here M and ? are the molality and the activity coefficient in the binary saturated solutions of the components 1 and 2 resp., while $?_i$ and $f_i$ are the activity coefficients of the components in the mixed liquid and solid phases being in equilibrium with each other after the formation of the mixed crystals. It is the $?_2/?_1$ and $f_1/f_2$ ratios that present the interactions between the components in the liquid and in the solid mixed crystal phase They are connected with the differences in the partial molar enthalpies of mixing as follows:

$$f_1/f_2 = \exp\left[(?\,\overline{H}_1 - ?\,\overline{H}_2)/RT\right] = \exp\left[\{a.f\,(?R/R\,) + b\,j\,(?\,e) + c?\,(?\,S)\}/RT\,\right]$$

The factors influencing the partial molar enthalpies of mixing are: the relative difference in size of the mutually substituting ions, atoms or molecules (?R/R), the difference in energy of interaction with their neighbours in the crystal structure (?e) and the difference in the energies depending on the spacial orientation of the chemical bonds (?S) e.g. in the case of open-shell ions with non-zero crystal field stabilization energy /1/.

Acknowledgment: The author is thankful to the Alexander von Humboldt Foundation for the 12th ISSP conference allowance.

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# SHORT COMMUNICATION

## NUMERICAL MODELING OF NATURAL BRINES IN THE SIX-COMPONENT OCEANIC SALT SYSTEM

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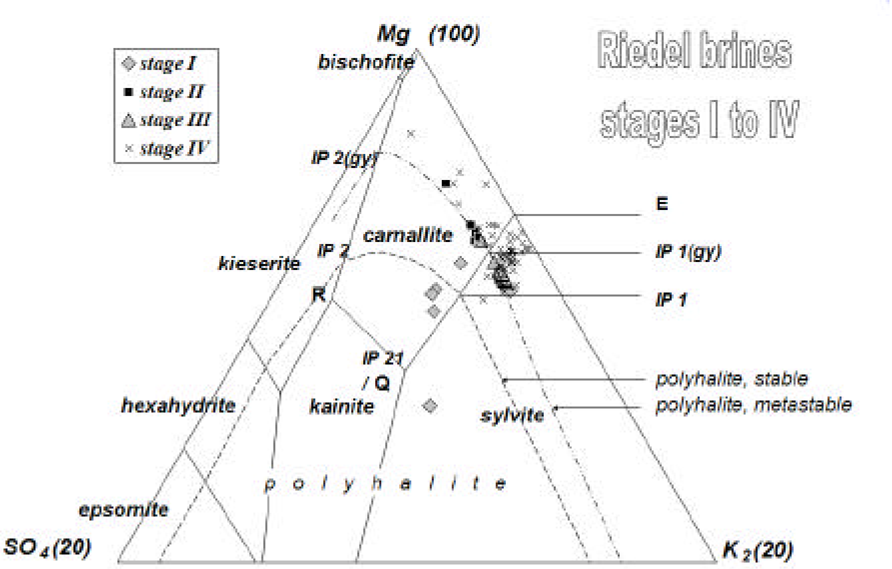
Evolution of natural magnesium chloride rich salt brines from seepages in a German potash mine was modelled [1] with the phrqpitz code [2]. The brine data reveal significant chemical changes during the 30 year period under investigation, which can be modelled by the invasion of external fluids, presumably cap rock brine, through the Stassfurt potash seam and the adjacent main anhydrite. In an initial rehydration stage, the paragenesis kieserite + anhydrite + sylvite reacted to form polyhalite + carnallite. However, temporary elimination of kieserite did not lead to a termination of the process in invariant point IP1, but instead continued to the metastable invariant point IP1(gy), with gypsum instead of anhydrite. Continued invasion of fresh cap rock brine produced univariant reactions along the carnallite-sylvite phase boundary and along the polyhalite phase boundary. Finally, elimination of polyhalite yielded solutions developing towards invariant point E of the degenerate quaternary boundary system.

The identification of the metastable processes around IP1(gy) was initially hampered by inaccurate older phase diagrams, linear approximations in more recent phase diagrams [3], lacking information on metastable equilibria, neglected Ca analyses, interference of post sampling dilution due to hygroscopic properties of concentrated magnesium chloride solutions giving misleading saturation indices, and reporting of brine analyses in terms of normalized standard salt components rather than elemental concentrations which precluded charge balance checks. These problems could be largely solved by using an internally consistent and accurate database [4] and phase diagrams based on this database for all operations, including newly calculated stable and metastable phase boundaries. Dilution effects were dealt with by plotting elemental ratios and by not using saturation indices.



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# SHORT COMMUNICATION

## CRITICAL EVALUATION OF SOLUBILITY RESULTS OF RARE EARTH CHLORIDES IN AQUEOUS SYSTEMS

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**Partly based on achievements of the late Tomasz Mioduski**

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Several important applications of rare earth chlorides in technology and science (catalyzers for organic synthesis and polymerization, production of alloys and compounds) induced investigations of the related aqueous binary and multicomponent systems.
Investigations of the solubility equilibria involving these chlorides in the ternary systems are very informative in connection with a formation of complex compounds (double salts, complexes, solid solvates) in such systems.

Experimental data on the solubility of chlorides of Sc, Y and La - Lu in water and in mixed aqueous solutions have been collected, compiled and critically evaluated. The most reliable values have been selected (see the table) as well as calculated from a general smoothing equation:
$\ln [x^{v} (1-x)^{v} (v+r)^{v+r} r^{-r} (1+x)^{-(v+r)}] = A + B/T + C \ln T + D T$
where x is the mol fraction solubility, r the number of water molecules in the equilibrium solid phase, v the number of ions produced upon the solute dissolution and T the absolute temperature.

The significant scatter of the experimental solubility results for several systems did not allow a selection of very precise solubility values for recommendation. The most uncertain are the data for the $ScCl_3$-$H_2O$ system. It is also difficult to suggest precise results for the $YCl_3$-$H_2O$ and $CeCl_3$-$H_2O$ systems. The solubility value of $PmCl_3$ in water is estimated here from an interpolation of the selected values of the solubilities of $NdCl_3$ and $SmCl_3$, and an assumption that the same type of the solid phase $LnCl_3 \cdot 6H_2O$ exists in the equilibrium conditions. Such procedure seems to be justified by the smooth decrease of the III-valent ionic radii and the smooth increase of the hydration energies of these elements.

The selected solubilities (in mol kg$^{-1}$) of rare earth metal chlorides in water at 298.15 K

| $ScCl_3$ | $YCl_3$ | $LaCl_3$ | $CeCl_3$ | $PrCl_3$ | $NdCl_3$ | $PmCl_3$ | $SmCl_3$ | $EuCl_3$ |
|---|---|---|---|---|---|---|---|---|
| 3.8 – 6.2 | 4.0 | 3.896 | 3.8 | 3.89 | 3.93 | (3.8) | 3.641 | 3.59 |
| $GdCl_3$ | $TbCl_3$ | $DyCl_3$ | $HoCl_3$ | $ErCl_3$ | $TmCl_3$ | $YbCl_3$ | $LuCl_3$ | |
| 3.59 | 3.57 | 3.63 | 3.69 | 3.78 | 3.88 | 4.00 | 4.12 | |

The solubility results were confronted with the experimental $LnCl_3$-$H_2O$ phase diagrams for ten elements obtained on the $H_2O$-rich sides between 200 and 450 K. This comparison allowed to reject many solubility results, as corresponding to metastable conditions. Some regularities in evolutional changes of the equilibrium solid phase compositions and the temperature ranges of their stabilities gave a basis for prediction of the equilibrium phase diagrams for the $PmCl_3$-$H_2O$, $HoCl_3$-$H_2O$ and $TmCl_3$-$H_2O$ systems, experimentally unknown so far. The $YCl_3$-$H_2O$ system is exeptional one showing a stronger tendency to immiscibility at higher temperatures than ones observed for other $LnCl_3$-$H_2O$ systems.

# SHORT COMMUNICATION

## ON HYDROXYAPATITE SOLUBILITY CONSTANTS, AT 298.15 K

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Hydroxyapatite is a solid phase with the theoretical composition $Ca_5(PO_4)_3(OH)$ that belongs to the *apatite* group. This structure can incorporate a variety of metal cations and anions, which changes the stability of the *apatite* structure. Even in vertebrates where it is found as the main mineral constituent of bones and teeth it exists as carbonateapatite containing small amounts of other ions as sodium, potassium or magnesium.

Applications of hydroxyapatite range from biomaterials to chromatography and environmental contaminants control. Solubility is an important parameter to be considered for some of these applications. A literature search on hydroxyapatite solubility constants in aqueous media, at 298.15 K, shows the dispersion presented in Figure 1.

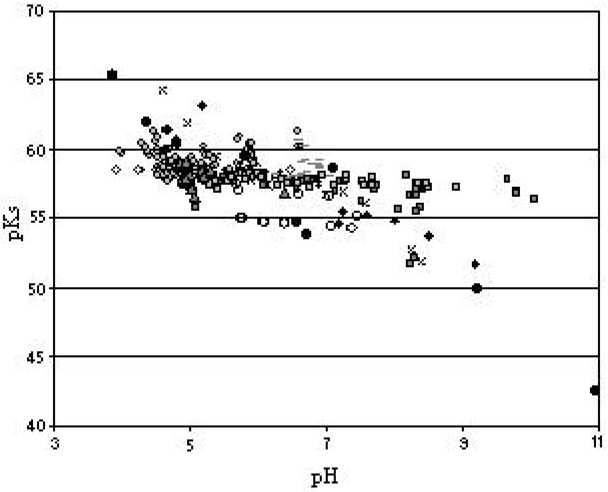

Fig. 1 - Variation of p*K*s with pH for a solid with the composition $(Ca_5(PO_4)_3(OH))$

The published broad range of values, more than twenty orders of magnitude between the lowest and the highest, induces questioning about the best value for the solubility constant of this solid phase. A pure statistical analysis of the data leads to the conclusion that the most likely value must correspond to that lying nearby the peak of the distribution curve. Will be this the best value? Which consequences arise from the use of it? How were the published values determined? Why a so broad range? An analysis of the published values will be done as well as a discussion of the most used and the situations they apply.

# SHORT COMMUNICATION

## MODELLING OF INORGANIC CHEMICAL SPECIES IN SURFACE POLLUTED WATERS

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The aqueous solution composition, ionic strength, acidity, redox potential and the proceeding chemical processes of oxidation-reduction and complex formation determine the different inorganic chemical species of macro, micro and trace elements existing in natural surface waters. The latter are under the influence of different natural phenomena, industrial, agricultural and daily human activities, which increase the species variety and cause water pollution since the chemical species determine the toxicity and bioavailability of elements in the ecosystem. Since there are no analytical methods for experimental determination of each species, monitoring investigations usually show the total content of the pollutants only. Thermodynamic modeling can be useful for that purpose.

A thermodynamic ion-association model (PHREEQCI computer program, version 2.11) was used for simulation of the species of major, minor and trace elements in different polluted surface waters of Bulgaria. The model uses the extension of the Debye-Huckel theory. The formation of each chemical species is defined by a mass-action expression with the appropriate association constant. The metal-ligand interactions define the activities of the different complexes in the solutions where the metal ions compete for coordination with the different anions or water molecules. The oxidation-reduction processes generate the species of the elements with variable oxidation states.

A new database *sst2005.dat* was used in our calculations. It was elaborated on the basis of the existing database *minteq.v4.dat*. The latter was upgraded with some more, thermodynamic constants concerning phosphate, nitrite, hydroxide, carbonate, sulfate, nitrate and chloride complexes, which are very important for surface waters. The result was more precise thermodynamic simulation of species distribution in natural waters, especially in the concentration range $10^{-20}$-$10^{-12}$ mol $kg^{-1}H_2O$, where metal phosphate, nitrite and carbonate species appear.

Acknowledgements: This work was done with the financial support of the EC FP6 PROJECT INCO-CT-2005-016414.

# SHORT COMMUNICATION

## CRITICAL EVALUATION OF ALKALINE EARTH CARBONATE SOLUBILITIES IN WATER

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Based on a compilation of aqueous solubility data of alkaline earth carbonates from the literature, a critical evaluation was conducted based on semi-empirical modeling and on thermodynamic modeling using a Pitzer model for ion activity coefficients. Primary literature data on the following species were investigated: magnesite ($MgCO_3$), nesquehonite ($MgCO_3.3H_2O$), lansfordite ($MgCO_3.5H_2O$), calcite, aragonite, vaterite ($CaCO_3$), strontianite ($SrCO_3$), and witherite ($BaCO_3$). Based on open-system data in the presence of a known $CO_2$ partial pressure, thermodynamic modeling was also used to estimate thermodynamic properties of the carbonates and their polymorph transitions. The model was restricted to data at $T < 100°C$ and $p(CO_2) < 2$ atm. The reason for this is the lack of a unique equation describing $CO_2$ solubility in water at all temperatures, and the lack of consistency in the high-pressure $CO_2$ solubility data. A critical evaluation, as well as thermodynamic modeling at higher temperatures and pressures is highly desirable because there is an increasing interest into deep underground aquifers as a storage medium for carbon dioxide as a technique to abate the greenhouse effect. Such storage can influence the solubility of carbonate minerals considerably. Thermodynamic properties of the calcium carbonate polymorphs were estimated simultaneously by forcing their relationships to be consistent with known phase transition data from the literature. Analysis of the data without this precaution would lead to unrealistic predictions of phase transition thermodynamics.

# SHORT COMMUNICATION

## PIPELINE CORROSION – CARBONATE SOLUBILITY IN MIXED SOLVENT ELECTROLYTE SYSTEM

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Many pipelines in the North Sea are made from mild steel. They are 16 inches in diameter and transport on average 4 million $m^3$ natural gas/day. A breakdown will be costly. Natural gas contains small amounts of $CO_2$. Produced gas is saturated with water (wet gas) and it condenses at the cold pipe wall during transportation. NaOH and glycol (MEG) or methanol is injected to prevent gas hydrate formation and corrosion. $CO_2$ dissolves into the water-MEG-NaOH liquid phase and the electrolytic environment will corrode the lower peripheral part of the pipeline. Various protective corrosion products are produced depending on the chemical environment. $FeCO_3$ is one of the corrosion products and the corrosion rate is very dependent on its saturation index. The ionic strength in these systems is very high due to the NaOH and an activity coefficient model is needed to calculate the carbonate activity.

In this work we seek to get a better understanding of $CO_2$ corrosion in natural gas pipelines through experimental work and modelling. Only few phase equilibrium data for the $CO_2$-NaOH-$H_2O$-MEG system have been published in the open literature. Solubility measurements have been performed and the extended UNIQUAC model [1-3] is being used for modelling the system. Figure 1 shows the model performance in pure water. Result will be shown for the mixed solvent system.

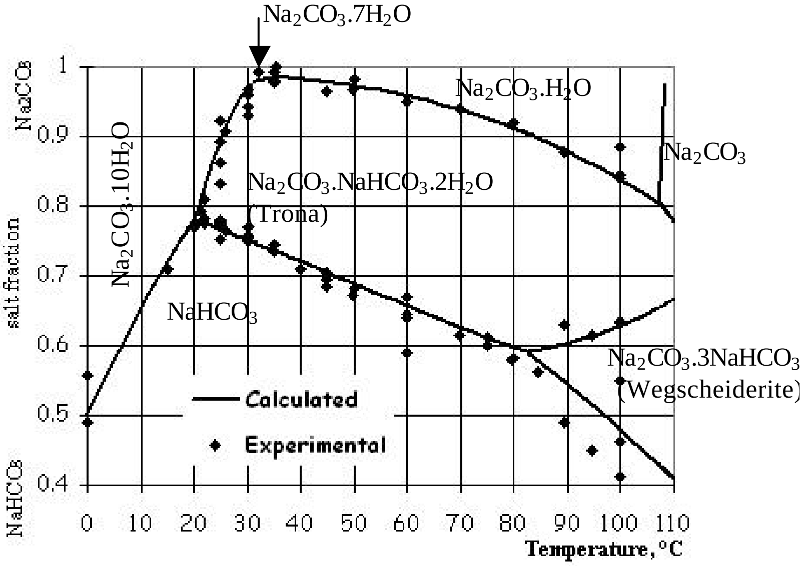

Figure 1: Phase diagram showing 2-salt lines in the ternary $NaHCO_3$-$Na_2CO_3$-$H_2O$ system as a function of temperature.

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## SHORT COMMUNICATION

### THERMODYNAMIC CONSISTENCY OF SOLUBILITY AND VAPOUR PRESSURE OF A BINARY SATURATED Salt + Water System: II. $CaCl_2$ + $H_2O$

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Solubility data of $CaCl_2 \cdot nH_2O$ (n=2,4,6) was predicted and evaluated by a Stokes and Robinson's adjusted BET-model using the vapour pressures of saturated soluion as criteria. Prior to the prediction, the BET model was parameterized with the most recently reported expermental osmotic coefficients (). The comparison with other model showed that, despite of fewer model parameters, the BET model can represent the activity properties of the the system $CaCl_2$-$H_2O$ the same good as the Pitzer model in a large temperature range from 298.15 K to 413.15 K. Meanwhile, experimental vapour pressure data of the saturated $CaCl_2$ solution was critically evaluated and some of them are selected as criteria for the solubility prediction. In principle, the predicted solubility has higher accurracy than a evarage set of various experimental data and therefore can be recommended for use in relevant cases.

# SHORT COMMUNICATION

## PHASE TRANSITION POINTS IN TERNARY AQUEOUS SYSTEMS

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Two-dimensional phase diagrams are widely used to describe, discuss and depict phase equilibria in chemical education, materials science and process technology. The common basis of these phase diagrams are Gibbs-Duhem equations with only three variable generalized forces (potentials) e.g. $p$, $T$, $\mu_i$, whereas all the others are held constant. Confirming and extending the conclusions of a previous communication [1] it will be shown in general that due to this common basis ternary aqueous electrolyte systems at constant temperature and pressure are analogous analytically as well as topologically to binary alloy, molten salt and slag systems. In particular eutonic (eutectic), peritonic (peritectic) and dystonic (dystectic) systems will be discussed. Figure 1a and 1b show a conventional solubility isotherm and the water activity vs. composition plot, respectively. The latter elucidates the eutonic-eutectic and dystonic-dystectic analogies, which do exist but can easily be overlooked in the conventional diagram.

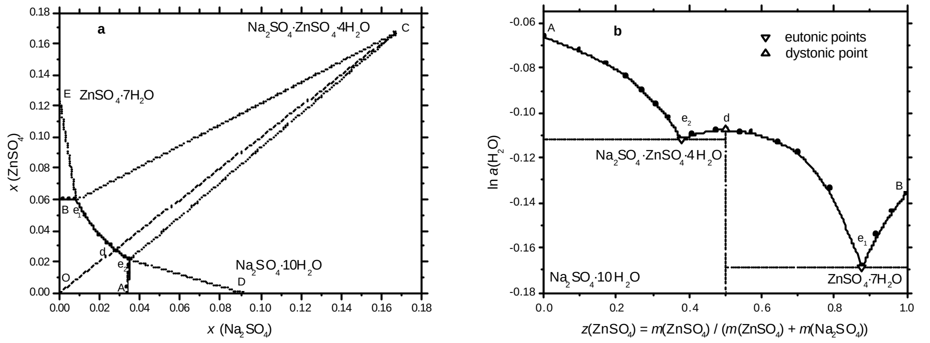

Fig. 1a and 1b. Solubilities in the system: $Na_2SO_4$-$ZnSO_4$-$H_2O$ at 25°C [2]. Points and solid lines: B-$e_1$ - solubility branch for $ZnSO_4$, solid phase $ZnSO_4 \cdot 7H_2O$; A-$e_2$ - solubility branch for $Na_2SO_4$, solid phase $Na_2SO_4 \cdot 10H_2O$; $e_1$-d-$e_2$ - solubility branch for ternary compound $Na_2SO_4 \cdot ZnSO_4 \cdot 4H_2O$. $e_1$, $e_2$ - eutonic points for three-phase equilibrium solid-solid-saturated solution. Dotted lines: boundaries of the fields B-$e_1$-E, A-$e_2$-D and $e_1$-$e_2$-C; tie-lines in these fields are not shown. Dashed line O-C: locus of points with $x(ZnSO_4) = x(Na_2SO_4)$ intersecting the solubility curve $e_1$-d-$e_2$ of the ternary compound at the dystonic point d. The chemical potential (or activity) of water decreases along B-$e_1$, increases along $e_1$-d, decreases along d-$e_2$, and increases along $e_2$-A.

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# SHORT COMMUNICATION

## TOPOLOGY OF SOLUBILITY ISOTHERMS IN TERNARY SYSTEMS ELECTROLYTE – ORGANIC SOLVENT – WATER

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Solubility in systems consisting of an electrolyte, organic solvent and water has been studied from several reasons. Among them, following are especially worth mentioning: the values of the solubilities themselves useful for separation processes (e.g. [1]), calculation of transfer energies of the electrolyte mostly from water to binary solvent or neat organic solvent ternary solution(s) (e.g. [2]), thermodynamics of the three phase equilibrium involving one solid and two liquid phases (e.g. [3]). In some cases also new mixed solvates are described and studied (e.g. [4]). During such investigations, the results are often not depicted in the shape of solubility isotherms and if so, only limited interest was devoted to general possibilities of the shape of the solubility isotherms, in spite of the fact that these possibilities are very versatile and it is the deeper insight to the topology of the title systems that makes more progress in understanding the structure and ionic processes in the respective systems possible.

A simple numerical system has been suggested to describe and classify the shapes of the solubility isotherms under consideration and the ways of getting comparative information about the ion solvation in the mixed solvents on this basis isotherms are discussed.

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# SHORT COMMUNICATION

## THERMODYNAMICS OF $Cu^{2+}/SO_4^{2-}$ ASSOCIATION IN AQUEOUS SOLUTION

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The interaction between $Cu^{2+}$ and $SO_4^{2-}$ in aqueous solution has often been regarded as a paradigm in the study of ion association. There are many reports of the stability constant of the $CuSO_4^0{}_{(aq)}$ complex but most of the published data refer to infinite dilution. Relatively little is known about the ionic strength dependence of the stability constant and in particular there have been no high quality potentiometric studies. The association between $Cu^{2+}$and $SO_4^{2-}$ in aqueous solution has therefore been investigated at 25°C and at ionic strengths from 0.05 to 5.00 M in $NaClO_4$ media using UV-Vis spectroscopy and copper ion-selective electrode potentiometry. The spectrophotometric stability constant is somewhat smaller than that obtained by potentiometry at all ionic strengths. This is thought to be due to the presence of solvent-separated $CuSO_4^0{}_{(aq)}$ ion pairs which are not fully detected by UV-Vis. The existence of such species was investigated by dielectric relaxation spectroscopy which showed significant concentrations of both double solvent-separated and solvent-separated ion pairs. The corresponding heat of reaction for the formation of $CuSO_4^0{}_{(aq)}$ was investigated in the same ionic media using titration calorimetry. Some of the difficulties in obtaining satisfactory results will be discussed.

# SHORT COMMUNICATION

## HEAT CAPACITIES OF CONCENTRATED SODIUM HYDROXIDE SOLUTIONS TO 300 °C

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Heat capacities of NaOH(aq) have been measured over a wide concentration range ($0.5 \leq m/\text{mol kg}^{-1} \leq 8$) at temperatures $323 \leq T/\text{K} \leq 598$ using a differential Calvet-type (Setaram C80) calorimeter at a pressure of 100 bar. Such solutions present special problems because of their aggressive nature. Brief descriptions will be given of the special modifications, operation and accuracy of the calorimeter. Experimental heat capacities per unit volume at constant pressure were converted to per unit mass values using density data measured recently in our laboratories by vibrating tube densimetry under identical conditions. This was necessary because of the inadequacy of existing density models of NaOH(aq) at high temperatures and concentrations. Apparent molar heat capacities, $C_{p\phi}$, for NaOH(aq) increase up to ~75 °C before decreasing dramatically at higher temperatures.

# PLENARY LECTURE

## HIGH-PRESSURE INVESTIGATION ON SOLUBILITY

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Solubility is one of fundamental properties for two components system as a function of temperature and pressure. But most solubility measurements have been done as a function of only temperature. We have applied pressure to them up to several hundred MPa. Several results will be shown.

**1. Inorgnic electrolytes (solid):** The most typical pair of solute and solvent for the solubility would be NaCl in water. It is often cited in text books of chemistry in high school. The first measurement under high pressures exceeding 150 MPa was done at 297 K by Cohen and Sinnige in 1910. After one century, we have extended the pressure up to 300 MPa and temperatures from 260 K to 323 K, taking the solute not only NaCl but also $NaCl?\,2H_2O$. The solubility of NaCl in water increased with increasing pressure and that of $NaCl?\,2H_2O$ decreased [1]. For other electrolytes of LiF[2], KCl[2], NaF[2], $K_2SO_4$[2], solubility in water increased with increaseing pressure. On the other hand, that of $ZnSO_4?\,7H_2O$[2], $(NH_4)_2SO_4$[2], CsCl[3], $NH_4Cl$[2,4], $NaBr?\,2H_2O$[5] decreased.

Following Le Chatelier-Braun's principle, solubility equilibrium has to shift to the state which has a smaller volume when a pressure is applied. And the volume occupied by a solute molecule in solution is thought to be larger than that in solid state because the solute molecule in solution have a space where it can move around. Therefore the solubility of a solid in solution should decrease with increasing pressure. But solubility of NaCl in water increased with increasing pressure. It is ascribed to a volume reduction of water around $Na^+$ and $Cl^-$ in $H_2O$ by electrostriction.

**2. Nonpolar organic compounds (solid)**: Solubility of naphthalene [6], anthracene [7], phenanthlene [7] in water was measured up to 200 MPa at 298.2 K. All of them decreased with increasing pressure following Le Chatelier-Braun's Law. Because of the low solubility of these compounds in water, pressure coefficient of the solubility, $x_S$, can be thermodynamically related to a volume change, $?V^{o}$, accompanying dissolution as shown in Eq. (1) and the $?V^{o}$ corresponds to the volume difference between the molar volume of a solid solute and the partial molar volume of the solute in water. As the former volume can be estimated from X-ray data of the solid, the partial molar volume in water can be obtained from the high-pressure solubility. The partial molar volume is usually estimated from the density measurement of the solution changing the concentration. But in the case of insoluble solute such as naphthalene in water, it is impossible to measure the density of aqueous solution of naphthalene changing the concentration. Then the high-pressure solubility is the only method to estimate the partial molar volume. Since Kauzmann (1959), though the volume change accompanying hydrophobic hydration has been thought to be negative value. On the contrary, comparison of the partial molar volumes of hydrophobic compounds, *i. e.*, napthalene, anthracene, and phenanthlene in water with those in oil phase shows that the sign of the volume change for hydrophobic hydration is not always negative [7].

$$(\ \ln x_S/?\ p)_T = -?V^{o}/(RT) \qquad (1)$$

**3. Polar organic compounds (solid)**: Solubility of several amino acids, *i.e.* glycine, alanine, valine, leucine, isoleucine [8], and monosodium glutamate monohydrate (MSG) [9], in water was measured under high pressures at 298.2 K. That of alanine, leucine, and MSG increased with increasing pressure, glycine decreased, and valine and isoleucine had a maximum. These variety in the high-pressure solubility is caused by a balance between the molar volume of the solid solute and the partial molar volume of the solute in water as described above, and the several solute-solvent interactions such as hydrogen bonding, electrostriction, affect to the partial molar volume.

**4. Nonpolar organic compounds (liquid) :** High-pressure solubility of benzene [10], toluene [10,11], ethylbenzene [10,11], propylbenzene [10,11], and *o*-, *m*-, and *p*-xylene [12] in water was measured. These aromatic hydrocarbons were used as model compounds for hydrophobic hydration. All solubility-pressure curves except for benzene and *p*-xylene had a maximum around 50-200 MPa. Benzene and *p*-xylene freezed before reached the maximum. Further we could obtain distorted solubility-pressure-temperature surfaces for toluene, ethylbenzene, and propylbenzene. Applying Eq.(1) to these solubility and using the molar volume of these liquid solutes at high pressures, we estimated the partial molar volumes of these alkylbenzenes in water as a function of pressure (up to 400 MPa) and temperature (273-323 K). The partial molar volumes increased with increasing pressure in low-temperature region and then decreased having a maximum at 50-100 MPa [13]. On the other hand, those in high-temperature region decreased with increasing pressure without any maximum. Such unusual negative compressibility of the partial molar volume in only low-temperature and low-pressure region may be caused by the hydrophobic hydration.

**5. New materials $C_{60}$**: "Discovery of new phenomena or new materials often makes us change our common sence in science." Fullerene $C_{60}$ is one of the new marerials, discovered by Kuroto and Smalley in 1985. High-pressure solubility of $C_{60}$ was first measured by us in 1999 [14]. The solubility both in hexane [14] and in toluene [15] increased with increasing pressure (though that of solvate in toluene decreased). Because $C_{60}$ is a nonpolar molecular solid, the solubility should decrease with increasing pressure as well as naphthalene but did not. The fact changes the old common sence that the solubility of nonpolar molecular solid in liquid should decrease with increasing pressure to new one. Following Le Chatelier-Braun's law, it is correct that solid $C_{60}$ (fcc form) is bulky compared with $C_{60}$ in toluene because the solubility increased with increasing pressure. Possible understanding for it is that there is a large vacant space among $C_{60}$ molecules in the solid because of the large molecular size of $C_{60}$ compared with that of solvent and the space diminishes when the solid is dissolved in the solvent.

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# PLENARY LECTURE

## METAL OXIDE SOLUBILITIES, SURFACE CHARGING, ION ADSORPTION AND DISSOLUTION/PRECIPITATION KINETICS IN HYDROTHERMAL SOLUTIONS

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The interaction of metal oxides (including silicates) with aqueous solutions at subcritical conditions has wide ranging applications in geoscience, environmental science, materials synthesis, corrosion in power plants and other industrial systems. The generalized solubility reaction of the oxyhydroxide of $Me^{z+}$ to its dissolved hydrolysis species is:

$$Me_xO_a(OH)_{xz-2a}(cr) + (y+a-xz)H_2O \Leftrightarrow Me_x(OH)_y^{xz-y} + (y-xz)H^+ \qquad (1)$$

For solutions at or near equilibrium with the stable or highly metastable oxyhydroxide, and particularly at elevated temperatures, the polynuclear dissolved species ($x>1$) are relatively unimportant, and the solution speciation is typically dominated by $Me(OH)_y^{z-y}$ ions with y varying from 0 to z+2, and complexes of these hydrolysis products with various ligands, such as carbonate, sulfate, organic anions, etc. This makes the solubility highly pH dependent, with slopes of $\log(\Sigma Me)$ vs pH near equilibrium varying from –z to +2 in the absence of complexing ions other than $OH^-$. The solubility minimum, corresponding to the equilibrium constant of the reaction to form the neutral species $Me(OH)_z^0$, can be strongly to very weakly temperature dependent, and varies with the intrinsic stability of the solid phase, with $K_{s,z}$ values ranging from ~$10^{-2}$ for amorphous silica to ~$10^{-11.5}$ for $ZrO_2$ at 150°C and vapor-saturation. The resulting V-shaped $\log(\Sigma Me)$ vs pH solubility profiles tend to shift to lower $pH_T$ with increasing temperature, and the "V's" become wider with increasing temperature and narrower with increasing salinity, due to the competing effects of the solvent dielectric constant and ionic strength on the activity coefficients of metal ions with absolute charge $\geq 1$. If the overall charge change for reaction (1) is near zero or can be minimized by appropriate addition or subtraction of the well-known dissociation of water, the ionic strength dependence of the equilibrium constant is minimized. For dissolution to the bare cation, $\log K_{s,0}$ is typically a linear function of 1/T(K) (e.g., near-zero heat capacity of reaction), but this is typically not the case for truly 'isocoulombic' reactions (no charge change). The pH values of zero net surface charge density of all metal oxides studied to date ($Al_2O_3$, $TiO_2$, $ZrO_2$, $Fe_3O_4$, $NiFe_2O_4$) decrease with increasing temperature from 25 to 250°C, paralleling closely the change in the neutral pH = ½$pK_w$, while the sorption affinities of cations on rutile ($\alpha$-$TiO_2$), the only solid phase for which extensive sorption data are available, increase strongly with temperature, paralleling the temperature dependence of the formation constant of $Me(OH)^+$ for the sorbing cation. In this talk, we will summarize a wide range of equilibrium and kinetically-controlled water-oxide interaction phenomena, emphasizing high-temperature *in situ* pH measurements and empirical modeling approaches.

# SHORT COMMUNICATION

## TERNARY WATER-SALT SYSTEMS WITH SUPERCRITICAL FLUID EQUILIBRIA – THEORETICAL DERIVATION AND EXPERIMENTAL STUDY

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The phase diagrams of constituent binary subsystems determine the major features of ternary phase diagrams since all binary equilibria spread into the three-component region of composition and take part in a generation of ternary phase behavior. Therefore the main types of phase behavior of binary subsystems can be used for preliminary systematization and derivation of the various classes of ternary water-salt systems [1, 2].

There are two main types of phase behavior for binary water-salt systems with solid-supercritical fluid phase equilibria. Binary systems of type **1** (such as $H_2O$ – KCl, $H_2O$ – $Na_2B_4O_7$, $H_2O$ – $K_2HPO_4$, $H_2O$ – $K_2CO_3$ etc) are characterized by increasing salt solubility with temperature and by the absence of critical phenomena L=G in solid saturated solutions. In the case of binary systems of type **2** (such as $H_2O$ – $Na_2CO_3$, $H_2O$ – $Na_2SO_4$, $H_2O$ – $Na_3PO_4$, $H_2O$ – $K_2SO_4$, $H_2O$ – $SiO_2$ etc), the salt solubility decreases with temperature under subcritical conditions, critical phenomena occur in equilibrium with solid salt (critical end-points "*p*"(L=G-S) and "Q"($L_1$=$L_2$-S)) and supercritical fluid equilibria (where the fluid is homogeneous at any pressure) take place in temperature range between points "*p*" and "*Q*". The following three classes **1-1-1**, **1-2-1** and **2-2-1** (designated by the types of binary subsystems) of ternary water-salt systems with binary anhydrous salt subsystems of type **1** are possible.

Attention will be focussed on the ternary systems of class **1-2-1** where supercritical fluid equilibria and critical phenomena in solid saturated solutions are spreading from the binary subsystem of type **2** and disappeared in three-component region. The results of theoretical derivation of such ternary phase diagrams and experimental data for the systems $H_2O$ – $K_2CO_3$ – $Na_2CO_3$, $H_2O$ – KCl – $K_2SO_4$, $H_2O$ – $K_2CO_3$ – $K_2SO_4$ and $H_2O$ – $K_2HPO_4$ – $K_2SO_4$ at high temperatures and pressures will be demonstrated and discussed. It is shown that various types of phase behavior in such ternary systems depend on the existence of immiscibility phenomena in binary subsystems of type **1** and a transition of metastable immiscibility region (spreading from the binary subsystem of type **2**) into stable equilibria.

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# SHORT COMMUNICATION

## SOLUBILITY OF URANIUM(VI) IN DILUTE TO CONCENTRATED $NaCl$, $MgCl_2$ AND $CaCl_2$ SOLUTIONS

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The assessment of the long time performance of a repository for nuclear waste is based on geochemical model calculations which require a comprehensive and reliable thermodynamic database. One option for the final disposal of nuclear waste is the storage in an underground repository located in a salt formation. For such repositories, the prediction of the radionuclide solubility and speciation in concentrated saline systems is of high importance.

Especially for alkaline or highly saline NaCl, $MgCl_2$ and $CaCl_2$ systems the knowledge of complex formation and the solubility limiting solid phases is very limited. We have therefore performed several independent sets of solubility batch experiments in carbonate free NaCl, $MgCl_2$ and $CaCl_2$ systems (22±2°C) covering the entire pH range and all relevant salt concentrations including brines with extremely high ionic strength (I ˜ 15). Special attention was dedicated to the identification and characterisation of the solubility controlling stable solid U(VI) phases using different complementary experimental techniques such as XRD, chemical analysis, TG-DTA and SEM-EDS.

In acidic to near neutral NaCl solutions, metaschoepite $UO_3{\cdot}2H_2O$(cr) is the stable solid phase. However, in alkaline solution a reproducible transformation into a thermodynamically more stable (and therefore less soluble) stoichiometrically well defined sodium diuranate phase $Na_2U_2O_7{\cdot}H_2O$(cr) is observed. The solubility of U(VI) in aqueous $MgCl_2$ systems is controlled by metaschoepite. In $CaCl_2$ solutions of high pH, metaschoepite is transformed into a calcium diuranate $CaU_2O_7{\cdot}3H_2O$(cr) not described before. In the neutral pH range becquerelite $CaU_6O_{19}{\cdot}11H_2O$(cr) is the solubility limiting solid phase.

The experimental data determined under conditions with metaschoepite as stable solid U(VI) phase are well described with the known hydrolysis constants recommended by the NEA-TDB [1] and yield a solubility product of log $K°_{sp}$ = -22.65 ± 0.13, which is similar to literature values from comparable solubility studies. The solubility data in the alkaline pH range are used to calculate the formation constants of the dominant anionic hydroxo complexes ($UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$), the solubility products of sodium diuranate $Na_2U_2O_7{\cdot}H_2O$(cr.) and calcium diuranate $CaU_2O_7{\cdot}3H_2O$(cr).

We have derived a comprehensive thermodynamic database (including log $K°_{sp}$ for the solubility determining solid phases, hydrolysis constants and ion interaction parameter (SIT, Pitzer) for the system U(VI)-Na-Mg-Ca-H-OH-Cl-$H_2O$ at 25°C. Model calculations based on this database are compared to experimental solubility studies at different ionic strengths.

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## SHORT COMMUNICATION

# PARTICLE SIZE EFFECTS ON THE SOLUBILITY OF M(III) AND M(IV) OXYHYDROXIDES

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Trivalent and tetravalent metal ions like $Fe^{3+}$ and $Th^{4+}$ or other actinide ions form X-ray amorphous hydroxides or hydrous oxides, microcrystalline and crystalline oxides, with the degree of crystallinity and the water content depending on the preparation method, temperature, and time of ageing. The solubility products of the different oxyhydroxide phases of a metal ion $M^{Z+}$ ($K_{sp} = [M^{Z+}][OH^-]^Z$), *e.g.*, those of fresh $Fe(OH)_3$(am) precipitates, ferrihydrite and hematite [1] or those of different Th(IV) oxides/hydroxides [2] vary by 5 - 7 orders of magnitude. The crystalline oxide, *i.e.*, $Fe_2O_3$(cr) or $ThO_2$(cr), may be considered as the only solid phase; hence the differences between the molar standard Gibbs energies of the oxide/hydroxide phases with particle or crystallite sizes in the range of d = 2 - 50 nm arise from the difference in molar hydrated surface. Knowing the thermodynamic data for the crystalline phase, usually from thermochemical data, its density, molecular weight, and the ionic radii, the increase of $?_fG°_m$ and $\log K°_{sp}$ with increasing molar surface, *i.e.*, decreasing particle size d, can be predicted with the equations of Schindler [3].

M(IV) oxide or oxyhydroxide solids used in solubility studies are usually not perfectly homogeneous with regard to their particle or crystallite size. The presence of different size fractions with different thermodynamic properties explains the unexpected pH-dependence of numerous experimental solubility data. For instance in solubility experiments with crystalline $ThO_2$(cr), the concentrations measured in the neutral and alkaline pH range approach those of amorphous $ThO_2{\cdot}xH_2O$(am), despite of the fact that the solubility constants derived at low pH differ by more than 6 orders of magnitude. Another example is observed for the solubility of amorphous oxyhydroxides at low pH where, contrary to the calculated strong pH-dependence, the experimental data often show an unexpectedly small dependence on pH.

The relation between standard Gibbs energy and particle size is also used to estimate a mean size of d = 1.5 - 2 nm for the polymeric/colloidal Th(IV) species present at a constant concentration level of about $10^{-6}$ M in solubility studies with $ThO_2{\cdot}xH_2O$(am) at pH > 6.

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# SHORT COMMUNICATION

## THERMODYNAMIC MODEL OF REE-FLUORITE SOLUBILITY IN HIGH-TEMPERATURE CHLORIDE FLUIDS

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Because fluorite is the most abundant REE-containing mineral at various types of deposits, its REE patterns appear to be an important numerical marker of physical-chemical conditions of ore formation. This study presents a thermodynamic model of coupled solubility of $CaF_2$ (a host mineral) and $(REE)F_3$ (admixtures) within the limits of approximation to the perfect solid solution. The known thermodynamic database SUPCRT98 together with free energies of individual REE-fluorides and HCH computer code [1] have been used for this purpose. The essence of model is a successive calculation of compositions of high T-P chloride fluids equilibrated with the REE-fluorite mineral association (as an accessory mineral) accompanied by initial quartz, Na-, Ca- and K-feldspars (as buffer minerals). The calculations have been carried out for the following basic P-T parameters of geochemically developing model fluid (°C/bar): 500/2000, 400/1000, 300/500, 200/250, 100/125. Its initial composition can be presented as 1kg $H_2O$+1m KCl+0.5m NaOH+0.05m HF. REE have been introduced into the system as a trace element in the form of $(REE)_2O_3$ to the extend of 0,001mol/kg $H_2O$ each.

Equilibrium concentrations (ppm) and pH in fluid.

| **T,°C** | **500** | **400** | **300** | **200** | **100** |
|---|---|---|---|---|---|
| **P,bar** | **2000** | **1000** | **500** | **250** | **125** |
| **pH** | **5.77** | **5.83** | **5.65** | **6.19** | **7.41** |
| F | 69.5 | 37.4 | 15.0 | 11.6 | 11.3 |
| Ca | 283 | 262 | 248 | 244 | 244 |
| La | 0.37 | $9\cdot10^{-3}$ | $3\cdot10^{-4}$ | $1\cdot10^{-4}$ | $1\cdot10^{-4}$ |
| Nd | 6.3 | 1.8 | 0.4 | 0.3 | 0.3 |
| Eu | 303.0 | 302.8 | 302.7 | 302.6 | 302.6 |
| Gd | 1.3 | $6\cdot10^{-2}$ | $4\cdot10^{-4}$ | $3\cdot10^{-5}$ | $8\cdot10^{-6}$ |
| Ho | 14.8 | 5.73 | 0.8 | 0.6 | 0.6 |
| Yb | 315 | 314 | 312 | 312 | 312 |
| Lu | 41.1 | 18.9 | 1.6 | 0.9 | 0.8 |
| Y | 0.26 | $2\cdot10^{-3}$ | $4\cdot10^{-6}$ | $8\cdot10^{-8}$ | $8\cdot10^{-9}$ |

The Table demonstrates the total F, Ca and REE equilibrium concentrations in fluid (in mg/kg $H_2O$). **Fig. 1** illustrates some regular decrease of REE fluoride contents (in mole fraction) in the matrix of the prevailing $CaF_2$ when the temperature and pressure of HF-containing chloride fluid decrease. An important point is that Eu behaves abnormally as compared to other REE in the framework of the elaborated model, which is in accordance with the data for natural REE-fluorite.

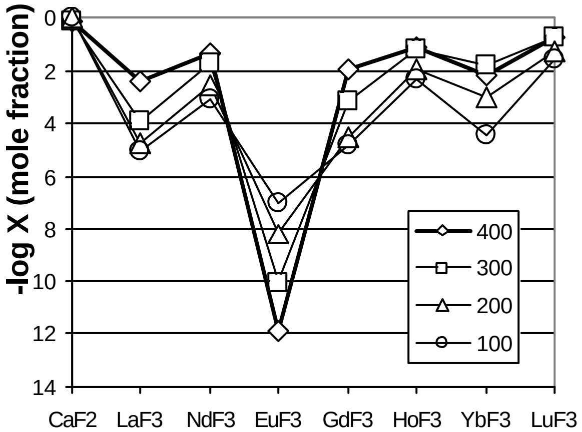

**Fig. 1.** The composition of the end REE-fluorite.

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# SHORT COMMUNICATION

## SOLUBILITY AND RE-PRECIPITATION OF NATIVE GOLD ON PYRITE SURFACE IN HYDROTHERMAL $H_2S$-$S^0$-BEARING SOLUTIONS AT 200 AND $250^0$C.

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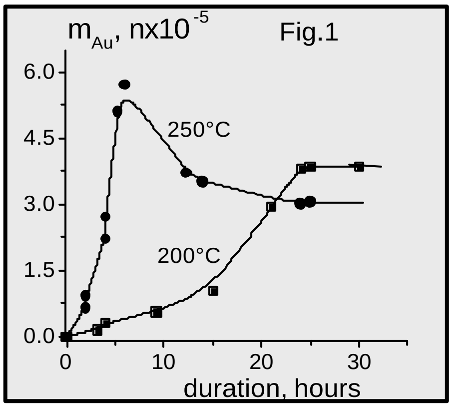
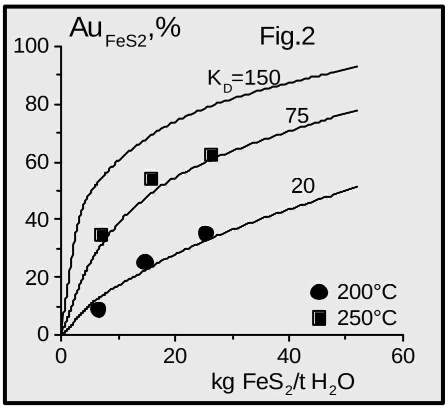
The study has been carried out to model the processes of Au concentration in sulfides during the mixing of hydrosulfide solutions and ocean waters at the bottom of ocean basins. Sulfide sulfur is partially oxidized to produce dissolved molecular sulfur and to create intermediate red-ox conditions (between pyrite-pyrrhotine and pyrite-hematite buffers) resulting in the maximum gold solubility. The autoclave method with mixing of solutions has been used for the experiments. $H_2S$ was oxidized up to $S^o$(aq) by the dosed quantities of $HNO_3$. The kinetics of Au(met) dissolution in the weakly acid sulfide solutions (t=200-250°C, P=150 bar, $0.1mH_2S+0.001mS^o+0.17mNaCl$, pH=3-5) demonstrates sharp increase of the process rate in moving from 200 to 250°C (Fig. 1). High value of activation energy of the gold dissolution process ($E_a$=83 kJ/mol) is indicative of kinetic regime of its limiting stage. It has been found that the relations between the dissolved forms of gold and sulfur conform to $Au(met) + 0.5H_2S(aq) + 0.5S^o(aq) = Au(HS)^o(aq)$ equilibrium. The value of gold solubility most closely corresponds to the calculated values if $G^o$ for $S^o$(aq) and $Au(HS)^o$ according to [1,2] are used.





A well-defined increase of Au(met) overall flow with increasing $FeS_2$ (liquid/solid ratio decreases from 128 to 30) has been determined on dissolving of gold in the presence of pyrite (fraction 20-40 mkm). A rise of the coefficient of gold distribution between pyrite and fluid with increasing temperature $K_D$ = Au($FeS_2$,ppm)/Au(solution, ppm) = 20±5 and 80±20 at 200 and 250°C, correspondingly has been revealed. This is favorable for deeper precipitation of gold on pyrite with increasing temperature and sulfide quantity (Fig. 2).

Grant of Ministry for Russian Science and Education DSP. 2.1.1.702
Grant RFBR 06-05-65042

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# SHORT COMMUNICATION

# A SIMPLE MODEL FOR COMPUTATION OF QUARTZ SOLUBILITY IN WATER-SALT-$CO_2$ SYSTEMS OVER A WIDE RANGE OF TEMPERATURES (0 – 1000°C) AND PRESSURES (1 – 10000 BAR)

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The system $SiO_2$ – $H_2O$ – salt is in many respects the main model system for studying hydrothermal equilibria. However, in spite of numerous experimental data there are no adequate quantitative models for the prediction of quartz solubility in ternary systems over a wide range of state parameters. The reason lies in the rather unusual behaviour of dissolved silica. Thus, at low temperatures (0 – 250°C) and at water-saturation pressures, increasing the salt content leads to the salting-out effect, which diminishes the $SiO_2$ solubility. Yet, as temperature approaches the critical point of water, the salting-out effect is superseded by a salting-in response. Similar behaviour has been recorded experimentally under supercritical conditions of $H_2O$. For instance, at 700°C and at constant mole fraction of NaCl, $x_{\mathrm{NaCl}} = 0.1$, lowering of pressure from 15 to 4 kbar at first simply reduces the salting-out effect, but later on ($P < 4$ kbar) the presence of NaCl increases $SiO_2$ solubility in comparison to the pure $H_2O$ solvent. Moreover, at low pressures the isotherm of $SiO_2$ solubility vs. salt content passes through a maximum: the salting-in effect at low $x_{\mathrm{NaCl}}$ evolves to salting-out at high salt concentrations. The intent of this study is to develop a simple model to explain this remarkably obtuse behaviour of silica solubility over a wide range of state parameters.

We propose the following equation to compute the molality of aqueous silica, $m_{\mathrm{SiO}_{2(aq)}}$, in equilibrium with quartz in water-salt-$CO_2$ systems:

$$\lg m_{\mathrm{SiO}_2} = A(T) + B(T)\lg\frac{18.0152}{V^*_{\mathrm{H_2O}}} + 2\lg x_{\mathrm{H_2O}}\,.$$

Here *A(T)* and *B(T)* are polynomials from Manning's equation for quartz solubility in pure water [1], and $x_{\mathrm{H_2O}}$ and $V^*_{\mathrm{H_2O}}$ stand for the mole fraction and effective partial molar volume of $H_2O$ in the fluid, respectively. The $V^*_{\mathrm{H_2O}}$ is computed using the expression $V_{mix} = x_{\mathrm{H_2O}}V^*_{\mathrm{H_2O}} + \sum x_s V_s$, where $V_{mix}$ is molar volume of mixed fluid (in $\mathrm{cm}^3\cdot\mathrm{mole}^{-1}$), and $x_s$ and $V_s$ denote mole fraction and intrinsic volume of the solute *s*, respectively. Adoption of $V_s$ values for NaCl (30.8 $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) and $CO_2$ (29.9 $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) permits satisfactory prediction of quartz solubility both in binary and ternary systems. In cases where experimental data are lacking, we have found that the $V_s$ value can be estimated on the basis of pure-substance properties.

This study was supported by grants of RFBR (05-05-66811) and Swiss Science Foundation (Project 200021-103905).

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# SHORT COMMUNICATION

## EXPERIMENTAL STUDY AND THEORETICAL EVALUATION OF THE THERMODYNAMICS PROPERTIES OF B(OH)$_{3,aq}$ AT SUPERCRITICAL CONDITIONS

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Neutral complexes are prevailing forms of migration of dissolved components in hydrothermal fluids of moderate and low density. At present there are very few experimental studies devoted to the thermodynamic properties of these species in low density fluids. Moreover, there is no reliable approach to describe the thermodynamic properties of aqueous components in a wide range of corresponding to both low and high densities of the solvent.

To determinate the thermodynamic properties of boric acid (B(OH)$_{3,aq}$) in low density solvent ($\rho \le 0.4$ g·sm$^{-3}$) takedaite (? ?$_3$(BO$_3$)$_2$) solubility was measured in pure water at 400°? and in the pressure range 100–1000 bars.

The dissolution of ? ?$_3$(BO$_3$)$_2$ can be described by the reaction:

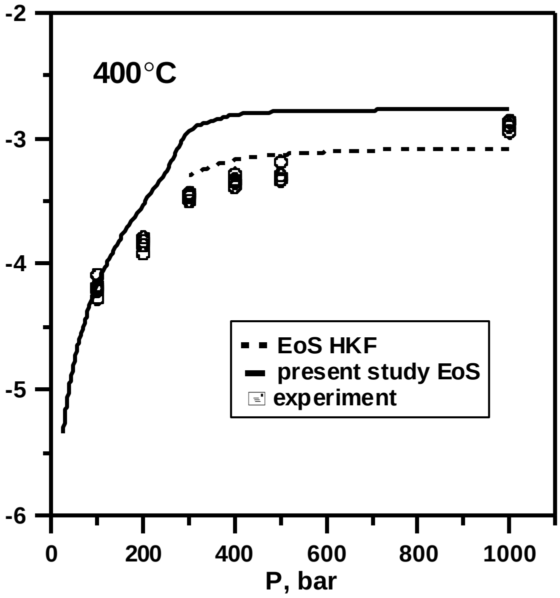
$$1/2Ca_3(BO_3)_{2,cr} + 3H_2O \Leftrightarrow 3/2Ca(OH)_2\downarrow + B(OH)_{3,aq}$$

Equilibrium solubility constraints the molality of B(OH)$_3$ in the fluid and thus specifies the thermodynamic properties of this species vs. fluid density.

Experiments were carried out in titanium alloy VT8 autoclave. At 1000 bar ($\rho = 0.7$ g·sm$^{-3}$) the equilibrium boron molality is in good agreement with the available thermodynamic data [1], that is lg $m$B(OH)$_{3,aq}$ = –2.89. Lowering pressure produces a decrease in boron content in the fluid.

A comparison of the experimental data and solubility values calculated using various EoS [1], [2] are shown in the figure.

The experimental data obtained will be employed to refine the empirical parameters of B(OH)$_3$ in the framework of EoS proposed by Akinfiev and Diamond for neutral aqueous species [2].



*This investigation was supported by RFBR (projects 04-05-65119 and 05-05-66811), the Program on Leading Scientific Schools (6722.2006.5) and international project NSERC-CRO.*

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# SHORT COMMUNICATION

## pH MEASUREMENTS AT HIGH TEMPERATURE: DETERMINATION OF THE HCl DISSOCIATION CONSTANT AT A TEMPERATURE OF 350° C AND 200 BARS OF PRESSURE

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The purpose of this work was to adjust the method of high-temperature pH measurements using the $ZrO_2(Y_2O_3)$ ceramic electrode and to determine the HCl dissociation constant ($K_{dis}$) at 350°C. The point is that $K_{dis}$ values obtained with different methods (mainly by the conductometric and solubility techniques) are widely scattered, especially near the critical point of low-density solutions.

The electrode system was calibrated in the acid pH range by HCl solutions with concentrations of $10^{-1}$-$10^{-4}$mol/kg$_{(H2O)}$ at 175, 250, and 300°C and 200 bars. The pH values of analyzed solutions were calculated using the SLOP98 thermodynamic database. At all temperatures, the slope of calibrated straight lines in the E-pH coordinates was close to the theoretical Nernst values (2.303*RT/n). It should be noted that the calculated pH values are virtually independent of the chosen $K_{dis}$ HCl value at the given temperature and concentration because the content of nondissociated $HCl^0_{(aq)}$ is negligible. Deviations of particular points from approximating straight lines do not exceed ±2 mV, which corresponds to an uncertainty of ±0.015 pH unit.

It is well known that, if the temperature rises to 350 C, the HCl dissociation constant notably decreases, and the association degree strongly depends on the acid concentration. Calculation indicates that, under these conditions (350 C and 200 bars), the pH value of a very diluted HCl solution ($10^{-4}$ *m*) virtually does not depend on the $K_{dis}$ accepted in the calculation. In more concentrated solutions, the chosen $K_{dis}$ value markedly affects the calculated pH value. In calculating the constant, we assume that (1) the slope in the E-pH coordinates at 350°C, as in the temperature range 175-300°C, remains theoretical and (2) the pH value of the $10^{-4}$ *m* HCl solution at 350°C and 200 bars is 4.022 (calculated on the basis of the SLOP98 thermodynamic database). This is enough to determine pH from the measured E values for the whole series of solutions ($3*10^{-4}$-0.1 *m* HCl). As a result, $pK_{dis}$ = 2.16±0.03 has been obtained.

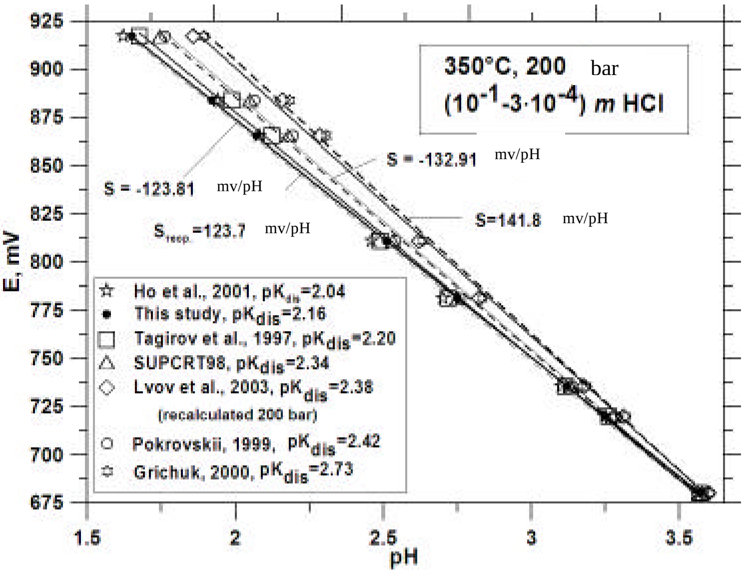

Fig.1. The slopes of experimental straight lines in the E-pH coordinates in dependence on the HCl dissociation constant at 350°C and 200 bars for HCl solutions (0.1-0.0003 *m*); lines are approximated with the least-squares method.

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# SHORT COMMUNICATION

## POSSIBILITIES OF HYDROMETALLURGICAL STRIPPING OF NON-CONCENTRATED CU-NI VALLERIITE ORES OF NORILSK ORE DISTRICT (NORTH SIBERIA) AT 90-150°C WITH THE USE OF $SO_2$ SOLUTIONS

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Valleriite with formula $2.0(Fe,Cu,Ni)S•1.41Mg(OH)_2•0.42Al(OH)_3$ is a mixed sulfide-oxide mineral containing (mass %) Fe – 25.8, Cu – 14.0, Ni – 0.85, S – 22.65, $Mg(OH)_2$ – 29.0, $Al(OH)_3$ –9.6 ( S101.9% - our data). It becomes a basic Cu carrier if valleriite amounts consist about 15-20% of the copper type sulfide ores of Norilsk deposits. Chemical and mineralogical compositions of Val-ore sample (mass %) are given below.

| **Fe** | Cu | **Ni** | **Co** | **S** | **CaO** | **MgO** | **MnO** | **$SiO_2$** | **$Al_2O_3$** | **S** |
|---|---|---|---|---|---|---|---|---|---|---|
| **19.8** | 3.9 | **1.37** | **0.046** | **12.9** | **4.2** | **23.2** | **0.041** | **17.0** | **3.84** | **86.3** |

| **Val** | Py | Cp | Mag | Po | Pn | **Serp** | Pg | Ca | **S** |
|---|---|---|---|---|---|---|---|---|---|
| **15.0** | 8.1 | 6.1 | 5.9 | 3.8 | 0.6 | **43.7** | 7.6 | 7.6 | 98.4 |

Val – valleriite, Py – pyrite, Po – pyrrhotine, Pn – pentlandite, Sept – serpentine, Pg – plagioclases, Ca – calcite.

The commercial value of Val-ore grows additionally due to the high content of platinum elements (Pt + Pd = 13.3 g/t). According to Fig. 1 the basic minerals Val (light veinlets) and Serp (gray background) add up to 60% and occur in the mineral intergrowths. This prevents the sulfide concentrates to be obtained by ordinary floatation.

Hydrothermal ore treatment in the flow regime has been carried out in water medium with 10% of $SO_2$ contained in the gas mixture (liquid/solid ratio is 3.5). At $P_{total}$ = 0.3÷0.5 MPa the flow rate of the gas mixture was 0.2-0.4 l/min per 20 g ore. Fig.2 demonstrates the dependence of the trapped $SO_2$ ($Q_{SO2}$, %) on its prescribed specific consumption ($Q_{SO2}$, g/g solid - gram $SO_2$ per 1 gram of initial ore). It can be seen that $Ex_{SO2}$ values must be about 90% in temperature interval 110-150°C if $Q_{SO2}$ = 0.2÷0.5. The intensive chemical interaction of ore components followed by $SO_2$ dissolution causes stripping of Val-Serp intergrowths due to serpentine dissolution and change of valleriite into covellite (CuS). As a result the produced solutions contain up to 50-145 g/l of (Mg+Fe). It is suggested that direct transformation of Val-Serp-ore should provide sufficient indicators at the next technological stages.

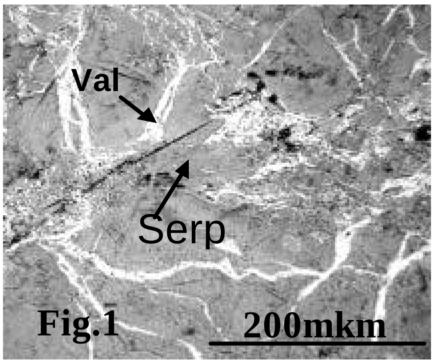

**Fig.1**

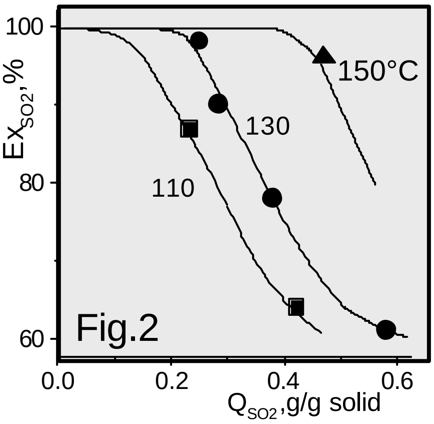

Fig.2

# SHORT COMMUNICATION

## SOLUBILITY Of $PbSO_4$ IN HIGH TEMPERATURE AQUEOUS SOLUTIONS

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The presence of trace amounts of lead (Pb) in steam generators (SG) has been identified to be a primary contributor to the premature stress corrosion cracking (SCC) of SG tubing. Lead-induced SCC (Pb-SCC) was first reported in 1965, and since then several cases of lead induced SG degradation have been found in power stations, with significant economic consequences, including station shutdown. Numerous and extensive laboratory studies worldwide have demonstrated a definite link between Pb and SCC of SG tube materials.

Data on the high temperature solubility of lead compounds are necessary to properly assess the nature of the lead species present under steam generator water chemistry. These data are especially important for steam generator crevices, where various impurities such as $Cl^-$ and $SO_4^{2-}$ can be highly concentrated. The lack of experimental data on the high temperature, pH dependant solubility makes it difficult to predict which lead species are most likely to cause or promote lead assisted corrosion or cracking, and how lead species are transported in steam generators.

In this paper, the experimental method used for the determination of Pb solubility at high temperature is described and some preliminary experimental results for $PbSO_4$ in high temperature aqueous solutions are also presented.

# PLENARY LECTURE

## SOLUBILITY OF SALTS IN WATER: KEY ISSUE FOR CRYSTAL GROWTH AND DISSOLUTION PROCESSES

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Abstract

The formation of salts from aqueous solutions both soluble and sparingly soluble as well as their dissolution, has attracted research interest I the past because of the wide spectrum of applications. Of particular importance is the formation and transformation of minerals exhibiting polymorphism, as in the case of calcium carbonate a salt encountered from geological formations to industrial scale formations. Of equal importance is the relative stability and transformation of mineral salt phases as in the case of calcium phosphates, found in several cases not only of biological mineralization but also in industrial scale formation. Understanding of these processes depends primarily on the equilibrium between the mineral phase considered and the aqueous medium in contact. Precipitation takes place in supersaturated solutions with rates depending on the solution supersaturation, i.e. the extent of departure from the equilibrium condition. The presence of foreign substances interacting at the solid/liquid interface is responsible for the kinetic stabilization of otherwise unstable mineral phases. The presence of organic compounds may favor the stabilization of vaterite during the precipitation of calcium carbonate. Heterogeneous nucleation on the other hand on polymeric substrates has been found to be decisive for the formation of specific polymorphs because of changes in the surface tension between the substrate and the forming new nucleus. The presence of water soluble organic compounds is responsible for the retardation both of the time needed for the onset of precipitation of struvite and for the kinetics of growth of the supercritical nuclei for the magnesium ammonium phosphate (struvite) system. Kinetics of crystal growth depend either on surface diffusion or on bulk diffusion which in turn is controlled by the medium fluid dynamics. It is interesting that dissolution processes are in some cases controlled by the same mechanism. In the case of calcitic marble, the dissolution of which is at least partly responsible for the deterioration of the building materials of monuments, the dissolution in alkaline aqueous media is controlled by surface diffusion. Compounds active at the marble/water interface may in this case be used as protective agents. In general, nucleation, growth and dissolution processes of inorganic salts depend on the solution supersaturation, the substrate/water interface and the fluid dynamics. The relative importance of these factors is directly related with the solubility of the respective salts.

# INVITED LECTURE

## PREFERENTIAL CRYSTALLIZATION IN THE 2 SOLID PHASE REGION

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Crystallisation is a suitable thermal unit operation for separation and purification of mixtures. The advantage of crystallization is the excellent distribution coefficient between the solid and the liquid phase because of the stereo specific integration into the crystal lattice. This advantage is limited through the occurrence of eutectics and compound formation. Usually the separation and purification is therefore done in the thermodynamical stable 2 phases area of the accordant solid phase and the corresponding fluid phase.

The *preferential crystallisation* (resolution by entrainment) uses the separation of one solid phase in the 3 phase area of the accordant solid phases A and B and the corresponding fluid phase. The requirements for using *resolution by entrainment* are a sufficient pronounced subcooling behaviour of the system and different crystallization kinetics of A and B in respect to nucleation and growth.

The advantages of this technique are separation at the eutectic composition, overcoming the eutectic point, increasing the process conditions for separation and improvement of the yield. This idea is the base to realize cycles which allows the separation of mixtures with eutectic behaviour. This technique is used e.g. for separation of optical isomers in lab scale for long times **GERNEZ 1866** and in newer times for large scale production e.g. of L-Menthol **MERCK 1966.**

The primary goal of the present work is the selective crystallisation of the solid phase A out of its stable area $S_A$-Fluid. Further the habit, the crystal size and the yield are investigated. The experimental investigations are done for 2 technical important substances: The structural isomers p-Cresol/m-Cresol and different Magnesium Sulfate Hydrates. The following parameters are investigated systematically: Phase of seeding crystals, composition of the feed, temperature of crystallization, crystallisation time and mass of seed crystals.

Seeding with p-Cresol shows e.g. at -4°C total crystallization of the melt till 40% mass fraction of p-Cresol, selective crystallisation of p-Cresol between 50% and 75% mass fraction p-Cresol and dissolution of the p-Cresol seed crystals between 40% and 45% mass fraction of p-Cresol.

For explanation of the results a hypothesis is used based on the assumption that during sub cooling the properties of the fluid phase liquids or melts keep conserved for a definite time. The kinetic of association and dissociation in the fluid phase is slow in respect to the crystallization kinetic.

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| | |
|---|---|
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# SHORT COMMUNICATION

## THERMODYNAMICS IN CRYSTALLIZATION OF ORGANIC COMPOUNDS

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Crystallization is a purification technique and separation process for most pharmaceutical and biological components. To understand crystallization processes the underlying solid-liquid equilibria (SLE) of the systems are of vital importance.

In this work, we consider aqueous and alcohol systems with organic compounds, in particular with amino acids. The calculation of the solubility is performed using the PC-SAFT equation of state taking into account the specific interactions (hydrogen bonding or dipole-dipole) between the molecules. For each binary system only one temperature-independent binary parameter is required. The solubility of amino acids in water-alcohol mixtures can then be predicted using only parameters from the binary sub-systems without fitting any additional data, as will be shown exemplary for glycine and DL-alanine in water-alcohol mixtures.

Using the knowledge of the acid-base behaviour of the amino acids, the pH-effects on solubility at different temperatures can also be predicted by the model. We will present the modelling results of pH-influence on the solubility of glycine, DL-alanine, and of DL-methionine in water at different temperatures.

Furthermore, the modeling of SLE for binary and ternary systems showing a solid-complex phase formation will also be discussed. Required is the molar composition (stoichiometry) of the solid complex. Successful description of SLE for the systems under study, e.g. methanol+water, phenol+acetamide, phenol+bisphenol A (BPA), as well as ternary system BPA+phenol+water, including the crystallization curves of the respective pure substances and the solid-complex phase by the PC-SAFT model with a single kij value for each binary system, is achieved.

# SHORT COMMUNICATION

## THERMODYNAMICS OF SOLUTION of NON-MESOMORPHIC SOLUTES IN THE *n*-HEXYL-*n*'-CYANOBIPHENYL (6CB) LIQUID CRYSTAL SOLVENT

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From specific retention volume measurements for 30 solutes (normal alkanes, branched alkanes, alkenes, hexadienes and benzene) at four temperatures in each of the nematic and isotropic phases of *n*-hexyl-*n*'-cyanobiphenyl (6CB), infinite dilution solute activity coefficients ($g_2^\infty$), solute partial molar excess enthalpies ($\overline{H}^e$) and entropies ($\overline{S}^e$) and partial molar enthalpies ($\Delta\overline{H}$) and entropies ($\Delta\overline{S}$)of solution were obtained [1] and analyzed in the light of an infinite dilution statistical model [2] to interpret the observed trends.

In this study these results were further analyzed to express $g_2^\infty$ as a function of the Flory-Huggins size effect correction ($g_{FH}^\infty$) and an interaction parameter ($k$); the sum of the thermal ($g_T^\infty$) and athermal ($g_{I-S}^\infty$) contributions to $g_2^\infty$. From regular solution theory solute ($d_2$) and solvent ($d_1$) solubility parameters were obtained at different temperatures for all the solutes in the nematic and isotropic solution phases.

Plots of $\Delta\overline{H}$ versus $\Delta\overline{S}$ were (see Table) reasonably linear. Such $\Delta\overline{H}$ - $\Delta\overline{S}$ compensation, reflects similar solute solubilities in the nematic and isotropic phases. Also an average ln $g_{2,N}^\infty$ / ln $g_{2,I}^\infty$ value of 1.077 ± 0.003 where $N$ and $I$ refer, respectively, to the nematic and isotropic phases, indicates lesser solute compatibilities with the nematic phase.

| Mesophase | Intercept / kJ mol $^{-1}$ | Slope / K | Correlation Coefficient |
|---|---|---|---|
| Nematic | – 2.66 | 293.4 | 0.947 |
| Isotropic | – 2.13 | 302.1 | 0.937 |

For all the solutes studied plots of $d_1$ versus temperature ($t$) showed a drastic and sharp change in $d_1$ at the nematic-to-isotropic transition (29.0 °C) which is reminiscent of enthalpy and density changes in first order transitions. The extent of the discontinuity in $d_1$ may thus be used as a measure of the strength of the transition while a continuous variation of $d_1$ across the phase transition would be associated with a second order transition. This finding can help in identifying second order transitions in liquid crystals or polymers. Currently results for *n*-octyl-*n*'-cyanobiphenyl (8CB) are being analyzed to test the nature of the much debated [3,4] smectic A-to-nematic transition of 8CB.

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# SHORT COMMUNICATION

## ELECTROLYTE SOLUTIONS IN SMALL PORES: MODELING OF FREEZING TEMPERATURE AND SOLUBILITIES

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The pressure generated by crystal growth of salts in confined spaces of porous building materials such as stone, brick and concrete is generally recognized as a major cause of damage in ancient monuments and modern buildings. Crystal growth is also considered as an important weathering mechanism of natural rocks in a variety of environments not only on earth, e.g. in deserts, dry Antarctic valleys and tropical coastlines, but also on Mars. Crystal growth in porous materials is the result of phase changes that are induced by variation of ambient temperature and relative humidity, *RH*. Unfavourable conditions of temperature and *RH* may result in repeated cycles of freezing–thawing, crystallization–deliquescence and hydration–dehydration, respectively. Under such conditions, building materials and natural rocks are subject to rapid decay.

In large pores, the relevant phase equilibria can be modeled using a multi-component electrolyte solution model such as the Pitzer ion interaction equations. It is then possible to predict ambient conditions, i.e. temperature and relative humidity that would minimize the frequency of occurrence of undesired phase changes inducing crystal growth in porous materials. For instance, model simulations are particularly helpful to predict the influence of changes in the room climate to salt contaminated masonry [1]. In very small pores, i.e. in pores $< 0.1$ µm, the situation becomes a lot more complicated. Firstly, the available pore space limits the maximum size of growing crystals and the interfacial energy of the crystal–liquid interface affects the solubility of dissolved species [2]. Secondly, in an unsaturated porous material, a curved liquid-vapor interface is formed resulting in a substantial pressure decrease which is given by Laplace's law. Hence, in addition to crystal size effects the influence of low pressure on the various phase equilibria has to be considered. The present contribution provides a discussion of the thermodynamic treatment of phase equilibria in unsaturated small pores including the vapor–liquid equilibrium, freezing temperatures and salt solubilities, first results are presented.

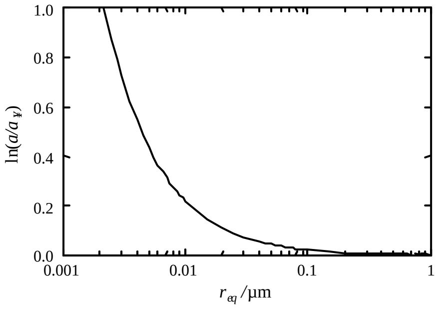

**Fig. 1** Solubility increase of small crystals

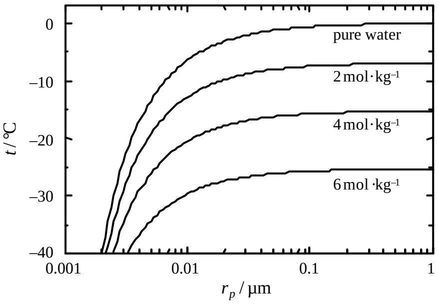

**Fig. 2** Freezing temperatures of NaCl(aq) in small pores

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# SHORT COMMUNICATION

## NUCLEATION AND MELTING TEMPERATURES OF SALT HYDRATES USED FOR HEAT AND COLD STORAGE UNDER STATIC PRESSURES UP TO 800 MPa

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Phase change materials (PCM) are used for efficient thermal energy storage in small temperature intervals. Inorganic PCM have a high storage density, but they tend to subcool. As the main advantage of PCM compared to sensible thermal storage is the operation in small temperature ranges, subcooling should be minimized.

Currently, subcooling is reduced by adding nucleators to the storage material. This method has two disadvantages. First, the nucleator can be deactivated when heated above its melting point. The reason is that the nucleator has a similar crystal structure as the PCM, therefore the melting points of the PCM and the nucleator are similar. Second, a proper nucleator has to be found for every storage material. For this search, no systematic approach has proven suitable yet. Usually, thousands of substances are tested without any guarantee for success.

From thermodynamic theory, it should be possible to initiate crystallization by applying high pressure to the subcooled melt. Compared to the use of nucleators, this method has two main advantages: The triggering mechanism cannot be deactivated by overheating the system. The method can be applied to a class of storage materials.

As a first step to develop a pressure based triggering system, we examined the nucleation under static pressure. For $NaOAc\cdot 3H_2O$, Rogerson et al. [1] derived from molecular theory that a pressure of about 700 MPa should shift the temperature of nucleation from -20°C to +20°C. Due to lack of experimental data, this prediction is based on many assumptions and simplifications, as well as on data of other materials.

Here, we present experimental data of $NaOAc\cdot 3H_2O$ under static pressures up to 800 MPa. We investigated the pressure dependency of the melting and crystallization temperatures. The melting curve is an important parameter for the theoretical understanding. The nucleation curve gives the pressure needed to initiate crystallization at ambient temperature. We observed a shifting of the nucleation temperature from -20°C at ambient pressure to +40°C at 800 MPa. This confirms that within this pressure range, the nucleation temperature of $NaOAc\cdot 3H_2O$ is shifted above room temperature.

Investigations of other salt hydrate PCM, namely calcium chloride hexahydrate $CaCl_2\cdot 6H_2O$ and potassium fluoride tetrahydrate $KF\cdot 4H_2O$, have also been conducted. Similar behavior was observed.

The focus of future investigations will be how long the pressure has to be applied and how this could be technically realized.

The experimental work was carried out at the high pressure laboratory of the Lehrstuhl für Fluidmechanik und Prozessautomation, at the Technische Universität München. This work was supported by German Federal Ministry of Education and Research (03SF0307A).

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## POSTER: A I 1

# EFFECT OF COPPER OXIDATION STATE ON THE TRANSFORMATION OF CHEMICAL SPECIES DURING SOLUTION – SOLID TRANSITION IN $CuX_n$– MX – $H_2O$ (X = $Cl^-$, $Br^-$; M = $Li^+$ – $Cs^+$) SYSTEMS

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Transformation of chemical species during solution – solid transition is one of the less studied problems of the Solution Chemistry. Copper allows the unique opportunity to undertake this investigation. The study of ternary copper halide systems enables us also to reveal the effect of heterovalent metal oxidation state on the solution properties including solubility. Copper(I) and copper(II) complexes with halide ligands are relatively stable in aqueous solutions and could be studied using different techniques. Moreover, multicomponent systems containing copper complexes are of great importance in many fields of application. They serve as photosensitive agents in photochromic and non-linear optics, catalyze many reactions of industrial and biological importance etc.

In this report the results of study of multicomponent $CuX_n$ – MX – $H_2O$ systems (n = 1, 2; $X^-$ = $Cl^-$, $Br^-$; $M^+$ = $Li^+$ – $Cs^+$, $NH_4^+$) are presented. To reveal the main regularities of transformation of chemical species during solution – solid transition the number of experimental methods was applied such as solubility, dilatometry, vibrational (IR and Raman) and EXAFS spectroscopy. The next aspects are under discussion:

1) effect of alkaline halides on the solubility depending on the copper oxidation state;
2) correlation between eutonic concentrations and the boundaries of the domination of different processes in solutions;
3) transformation of copper species during solution – solid transition;
4) precursors of copper double salts formation.

The results obtained show that strong complexation determines qualitative similarity of solubility isotherms for all the systems containing copper(I) once competition of hydration and ionic association with complexation of copper(II) determines far better pronounced difference between $CuX_2$ – MX – $H_2O$ systems. Weak effects of structural transformation during solution – solid transition in CuX – MX – $H_2O$ compare to $CuX_2$ – MX – $H_2O$ systems confirms the leading role of copper complexation in solid phase formation. It was established by EXAFS data the formation of $CuX_n$ (n>3) complex anions is the necessary condition for the double salts crystallization in all ternary systems under study. Copper chemical species dominating in saturated solutions strongly depend on outer–sphere cation.

Acknowledgement: RFBR (project 05-03-32099a) and INTAS (Programme of INTAS fellowships for young scientists, project 04-83-3830) are thanked for the financial support.

# POSTER: A I 2

## EFFECT OF LOW FREQUENCY SONICATION ON THE SOLUBILITY OF $CuCl_2$, $CuSO_4$ AND $MgSO_4$ IN WATER AT 25 $^{?}$?

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In this report the comparative analysis of the effect of low frequency (45 – 105 Hz) acoustic field on the properties of aqueous solutions is presented. Aqueous solutions of magnesium and copper sulfates were chosen for this study that enables us to reveal the effect of covalency of metal – water bonding. To study the effect of acidocomplexation, the data were compared with those for copper dichloride.

First of all, the low frequency sonication of saturated solutions results in substantial (up to 17%) growth of the solubility of all the salts under study. We have shown that solubility is the periodic function of sound frequency, where position of principal maximum and relative growth of the function change contrary to the hydration energy of the salt: $CuSO_4 > MgSO_4 > CuCl_2$.

The next reasons lead to the observed effects:

1) At sonication the change of solution structure takes place. Therefore, the more is ionic hydration ($SO_4^{2-} > Cl^{-}$, $Cu^{2+} > Mg^{2+}$), the higher energy is required to change ionic environment;

2) The more is structure-making effect of ion ($SO_4^{2-} > Cl^{-}$, $Cu^{2+} > Mg^{2+}$), the higher is activation energy of the conformational transitions in solution. Therefore higher frequency of sound waves is required to change conformations of water clusters;

3) The presence of a set of chloride complexes in solution of copper dichloride results in less order in solution that also makes the structure more labile;

4) concentration of saturated solution decreases from $CuCl_2$ to $CuSO_4$ that increases the number of water molecules unperturbed by ion. That results in increase of the probability of formation of cavities in structure of liquid water and in dissolution of padding amount of salt.

To study this phenomena more detailed we have undertaken spectroscopic study of these solutions using electron absorption spectroscopy and IR spectroscopy (double-difference technique). It was established that sonication results in decrease of absorption once the position of absorption maximum remains the same. This result agrees fairly well with the suggestion that sonication affects on bulk water and outer hydration shall whereas the local environment of ions remains nearly unperturbed. This leads also to the significant change of hydrogen bonding in solution that is confirmed by the results of IR spectroscopic study (frequencies of O – D stretching vibrations decrease on 120 $cm^{-1}$).

Conclusions:

– Sonication results in significant structural transformation of aqueous solutions of the salts under study and has “structure-making” effect:

– Solution properties periodically depend on sound frequency applied:

– After removal of acoustic field more slow relaxation compare with ultrasound effect is observed for the low frequency sound waves.

Acknowledgements: Russian Found of Basic Research (grant 05-03-32099a) is thanked for the financial support.

# POSTER: A I 3

## (SOLID + LIQUID) METASTABLE EQUILIBRIA IN QUATERNARY SYSTEM $Li_2SO_4 + Li_2CO_3 + Li_2B_4O_7 + H_2O$ at 288 K

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**Abstract:** Metastable equilibrium solubilities and densities of the solution in the quaternary system $Li_2SO_4$ + $Li_2CO_3$ + $Li_2B_4O_7$ + $H_2O$ at 288 K were determined experimentally. According to the experimental data, the metastable equilibrium phase diagram was plotted. In the phase diagram(Figure 1), there are one invariant point F, three univariant curves E1F, E2F and E3F, three fields of crystallization: $Li_2SO_4$•$H_2O$(BE1FE2), $Li_2CO_3$(E1FE3A), $LiBO_2$•$8H_2O$ (E2FE3C). There are no solid solutions or double salts formed in the quaternary system at 288 K. Lithium carbonate ($Li_2CO_3$) has bigger crystallization field than others. The large crystallization region in the phase diagram indicates that lithium carbonate are of low solubility, therefore, most lithium carbonate ($Li_2CO_3$) can crystallize from solution easily. Crystallization field of lithium borate was $LiBO_2$•$8H_2O$ at 288 K in metastable equilibrium for the quaternary system, which were $Li_2B_4O_7$•$3H_2O$ in stable phase equilibrium at 288 K. Lithium sulfate ($Li_2SO_4$) has the highest concentration and strong salting-out effects on other salts in the system.

**KEYWORDS:** Metastable Equilibrium, Borate, Sulfate, Solubility

### Acknowledgements

The project was supported by the National Nature Science Foundation of China (No. 40303010).

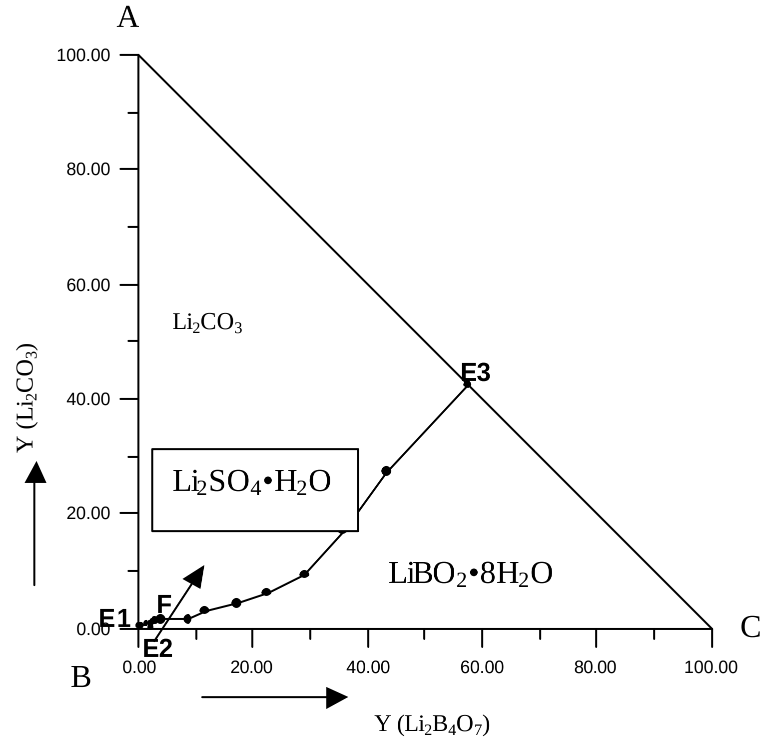

**Figure 1 Metastable equilibrium phase diagram of the quaternary system at $Li_2SO_4$ + $Li_2CO_3$ + $Li_2B_4O_7$ + $H_2O$ at 288 K**

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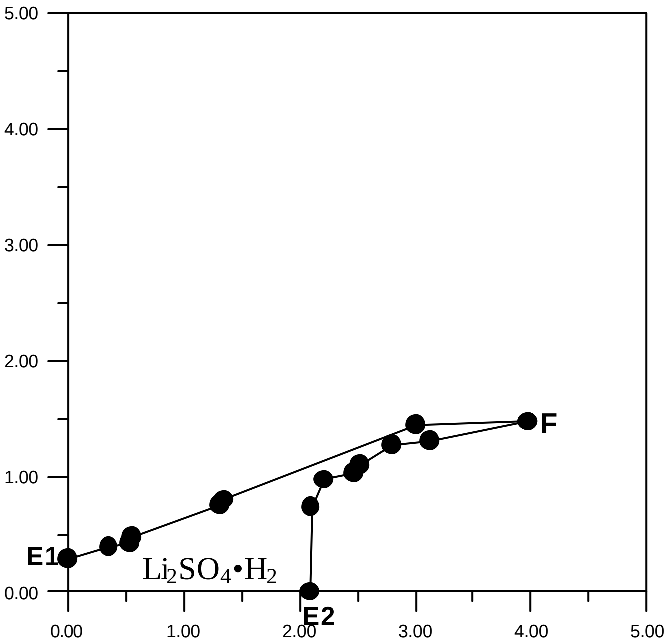

**Figure 2. Enlarged partly phase diagram of the quaternary system $Li_2SO_4$ + $Li_2CO_3$ + $Li_2B_4O_7$ + $H_2O$ at 288K**

# POSTER: A I 4

## SOLUBILITY OF POTASSIUM HEXAFLUOROSILICATE IN ELECTROLYTE SOLUTIONS

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Hexafluorosilicic acid, $H_2SiF_6$, and its salts, hexafluorosilicates, play an important role for example as initial substances, by-products or intermediates in fluorine chemistry. The low solubility of $K_2SiF_6$ is often used in analytical chemistry for the determination of hexafluorosilicate contents of solutions.

The aim of our investigations was to understand the behaviour and interactions of the ion $SiF_6^{2-}$ in strong electrolyte solutions because the occurring equilibria are quite complex. Therefore we decided to determine the solubility of $K_2SiF_6$ (at 25°C) in different acids HF, $H_2SiF_6$ and $HNO_3$. Moreover the solubility curves of $K_2SiF_6$ in potassium salt solutions (KF and $KNO_3$) are investigated.

The solubility experiments were carried out by stirring the solutions with the suspended solid phase for days or weeks at constant temperature. After that the remaining solid $K_2SiF_6$ was filtered, dried and weighed. The solubility plotted against the electrolyte molality shows substantial differences for the various electrolytes. Higher HF and $HNO_3$ concentrations lead to an increasing solubility of $K_2SiF_6$. $H_2SiF_6$ first lowers the solubility and at higher $H_2SiF_6$ contents the solubility of $K_2SiF_6$ slightly increases.

As expected in potassium salt solutions the solubility of $K_2SiF_6$ is decreasing with the salt content. Besides that at a certain concentration of $KNO_3$ a new solid phase was found: $K_2SiF_6 \cdot KNO_3$. The crystal structure of this double salt was solved by a single crystal diffraction study.

The resulting solubility data in combination with other available thermodynamic data will be used to establish a thermodynamic model based on PITZER or SIT theory with which equilibria in strong and concentrated electrolyte solutions can be described.

# POSTER: A I 5

## SOLUBILITY RELATED TO SUBSTITUTED POLYHALITES

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Polyhalite $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$ represents a common mineral in salt rocks. Analogue triple salts have been prepared earlier, where Mg is substituted by Mn, Fe, Co, Ni, Cu, Zn. We are interested in the crystallization field of these polyhalite analogues.

Since polyhalite forms very slowly at room-temperature 40°C were chosen for the experiment. An investigation of the crystallization field of polyhalite was started. Compared with data at 35°C a noticeable enlargement of the existence field can be seen within these 5 K.
All other crystallization fields will be estimated on the basis of thermodynamic models. Literature search for interaction parameters or relevant data revealed a main data lack in the systems $MSO_4$-$CaSO_4$-$H_2O$ (M = Mn, Co, Ni, Cu, Zn). Therefore, investigations on these systems were started. So far the systems $CaSO_4$-$MSO_4$-$H_2O$ (M = Ni, Zn) were examined over a wide concentration range at 25°C. With increasing molality of the heavy metal sulfate the solubility of gypsum $CaSO_4 \cdot 2H_2O$ decreases first and then rises to a maximum. The variation of the solubility curves in dependency on the nature of the $M^{2+}$ ion can be interpreted by the effect of ion pair formation. Calculation of the mean ionic activity coefficient ?$_{\pm}$($CaSO_4$) from the solubility data in the 3 systems yields increasing values going from the $ZnSO_4$ to the $MgSO_4$ system. This coincides with increasing ion pair formation constants $K_{ZnSO4} < K_{NiSO4} < K_{MgSO4}$ and thus the solubility curves reflect competition of ion pair formation with $CaSO_4°$.

Calorimetric measurements were started to determine the heat of solution of polyhalite at 25°C. The experiment will allow calculations of the equilibrium constants of formation from data at 40°C, where the experiments are performed, to 25°C. From preliminary measurements a heat of dissolution at infinite dilution of -23,47 kJ/mol at 25°Cwas derived.

# POSTER: A I 6

## SOLUBILITY OF SODIUM CHLORIDE IN WATER IN DEPENDENCE OF PRESSURE

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The temperature dependence of the solubility of sodium chloride belongs to one of the best documented of all ionic compounds [1]. However, data on pressure dependence are sporadic and scattered. Since the pressure effect on solubility is small very high pressures had been applied in measurements in the past. Most recent investigations from Matsuo and Sawamura [2] cover a pressure range up to 600 MPa. For NaCl the solubility increases with pressure, which is quite particular for a very soluble salt.

For an understanding of long-term solution-dissolution processes in evaporitic sediments the small variations of solubility due to pressure changes up to 20 MPa are relevant and have to be known quantitatively. However, in this pressure range experimental data are not available.

Pitzer, Peiper and Busey [3] developed a complex thermodynamic model for the system $NaCl-H_2O$, which should be valid between 273 – 573 K and up to 100 MPa. It is based on an extended form of Pitzer‘s equations and involves more than 120 adjusted parameters. Estimations of the pressure effect from this model give relative variations in solubility of approx. 0.03 % per 1 MPa pressure change. This corresponds to a an absolute value of 0.13 g NaCl/kg $H_2O$ at a saturation concentration of 360 g NaCl/kg $H_2O$. The same variation in solubility would be caused by a temperature change of 0.06 K.

An apparatus and experimental procedure has been developed, which is based on a quasi-flow technique using a HPLC pump and ensures the quantitative determination of small solubility changes at high absolute values of solubility.

In this paper the experimental solubility data at 25, 40 and 80 °C are reported and discussed in the context of accuracy, experimental methodology and agreement with the Pitzer-Peiper-Busey model. Conclusions are drawn in respect to re-crystallization processes in evaporitic sediments and safety aspects for radioactive or toxic disposals in deep rock salt formations.

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# POSTER: A I 7

## METAL PHOSPHONATE CHEMISTRY: FROM SYNTHETIC CURIOSITIES TO REAL INDUSTRIAL AND BIOMEDICAL APPLICATIONS

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Metal phosphonate chemistry is going through a renaissance in the last decade. Synthetic chemists, chemical engineers, pharmacists, medical doctors, water technologists, and application scientists have been working on this exciting area of technology from different perspectives. Metal phosphonate chemistry has found numerous applications in the areas of chemical water treatment, pharmaceutical science, ion exchange, catalysis, medicine, agronomy, etc.

In this contribution the synthetic and structural chemistry and applications of metal phosphonate materials are presented with emphasis on alkaline earth metal phosphonates. In particular synthetic methodologies will be presented for a plethora of M-phosphonates (M = Mg, Ca, Sr, Ba and Zn, see Fig. 1) [1]. Structurally diverse phosphonate ligands include di-, tri- and tetra-phosphonates and mixed phosphonates/carboxylates [2].

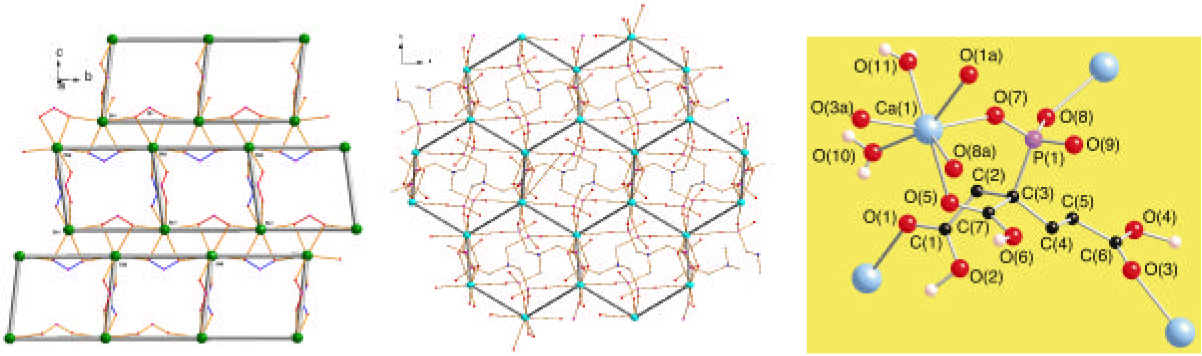

Fig. 1: Structure fragments of $\{Ba(H_4AMP)(H_2O)\}_n$ (left) and $[Sr(H_4AMP)]_n$ (center), AMP = amino-tris-methylenephosphonate, and $[Ca(H_3PBTC)(H_2O)_2 \cdot 2H_2O]_n$, PBTC = 2-Phosphono-butane-1,2,4-Tricarboxylic acid (right), coordination polymers.

Methods of structural characterization are also mentioned. Lastly, the role of these metal phosphonates in modern, ground breaking application areas is discussed. These areas of research in our laboratories include chemical water treatment [1], oilfield drilling, desalination, scale inhibition, corrosion inhibition [2], dissolution [3], dispersion, treatment of osteoarthritis and related pathological conditions [4], and others [5].

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# POSTER: A I 9

## SOLUBILITY MEASUREMENTS OF TERNARY SYSTEMS BY ISOPIESTIC METHOD

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Idea to use isopiestic method to determine solubility in ternary systems is not a new one. Kirgintsev and Trushnikova seem to be first persons who did it [1]. Then Platford applied the technique to somewhat more complex systems [2]. Compositions of invariant (T, P = const) points were determined in all cases. Toward this end an extra cup is placed into isopiestic chamber together with the set of homogeneous ternary solutions. This extra cup contains an excess of heterogeneous composition (saturated solution and two solid phases) corresponding to the invariant point. On achieving isopiestic equilibrium, the compositions of initially homogeneous solutions are determined in the usual fashion (by weighing). These compositions form two straight lines in the solubility diagram with intersection point corresponding to the composition of liquid phase of invariant point under investigation. Reverse direction of the straight lines also allows determining the composition of equilibrium solids.

The main advantage of the technique is the high accuracy of determination of compositions of all three phases, as it does not require the chemical analysis of ternary mixtures. It should be noted that there are variants of the considered method, which include partial chemical analysis of equilibrium compositions (see, for example, [3]), but consideration of such techniques is outside the present report.

The method has two main disadvantages. First, it is a time-consuming (one point takes a week or two). Second, it is necessary to prepare heterogeneous composition for an extra cup. It does not cause any problem if a congruent invariant point (euthonic point) with solid phases of constant composition is studied. The investigation of incongruent invariant point (perithonic point) may be somewhat more difficult. Moreover, an unsolvable problem may occur on the investigation of invariant point with solid solution crystallization, as the preparation of the heterogeneous composition requires knowing the composition of all three equilibrium phases beforehand.

However, we can essentially eliminate the disadvantages of the method considered, with the advantages being kept. The modified technique includes the repeatable process. The set of ternary solutions achieves isopiestic equilibrium in the first stage. A part of solvent is removed from the solutions by evaporation in the second stage. Then both stages are repeated. Usually the process is stopped when homogeneous solutions reach the saturation limit of any solid phase. However, the continuation of the mentioned process gives a lot of valuable information on solubility. The following systems are presented as examples: $K_2SO_4$ – $CuSO_4$ – $H_2O$ (the solubility curve of a double salt), $(NH_4)_2SO_4$ – $Cs_2SO_4$ – $H_2O$ (the phase diagram of a system with crystallization of solid solution sets), and $MgCl_2$ – $FeCl_2$ – $H_2O$ (this example answers the question: Whether solid phase has constant composition or whether it is a limited solid solution?).

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## POSTER: A I 10

# NUCLEATION AND MELTING TEMPERATURES OF SALT HYDRATES USED FOR HEAT AND COLD STORAGE UNDER STATIC PRESSURES UP TO 800 MPa

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Phase change materials (PCM) are used for efficient thermal energy storage in small temperature intervals. Inorganic PCM have a high storage density, but they tend to subcool. As the main advantage of PCM compared to sensible thermal storage is the operation in small temperature ranges, subcooling should be minimized.

Currently, subcooling is reduced by adding nucleators to the storage material. This method has two disadvantages. First, the nucleator can be deactivated when heated above its melting point. The reason is that the nucleator has a similar crystal structure as the PCM, therefore the melting points of the PCM and the nucleator are similar. Second, a proper nucleator has to be found for every storage material. For this search, no systematic approach has proven suitable yet. Usually, thousands of substances are tested without any guarantee for success.

From thermodynamic theory, it should be possible to initiate crystallization by applying high pressure to the subcooled melt. Compared to the use of nucleators, this method has two main advantages: The triggering mechanism cannot be deactivated by overheating the system. The method can be applied to a class of storage materials.

As a first step to develop a pressure based triggering system, we examined the nucleation under static pressure. For $NaOAc \cdot 3H_2O$, Rogerson et al. [1] derived from molecular theory that a pressure of about 700 MPa should shift the temperature of nucleation from -20°C to +20°C. Due to lack of experimental data, this prediction is based on many assumptions and simplifications, as well as on data of other materials.

Here, we present experimental data of $NaOAc \cdot 3H_2O$ under static pressures up to 800 MPa. We investigated the pressure dependency of the melting and crystallization temperatures. The melting curve is an important parameter for the theoretical understanding. The nucleation curve gives the pressure needed to initiate crystallization at ambient temperature. We observed a shifting of the nucleation temperature from -20°C at ambient pressure to +40°C at 800 MPa. This confirms that within this pressure range, the nucleation temperature of $NaOAc \cdot 3H_2O$ is shifted above room temperature.

Investigations of other salt hydrate PCM, namely calcium chloride hexahydrate $CaCl_2 \cdot 6H_2O$ and potassium fluoride tetrahydrate $KF \cdot 4H_2O$, have also been conducted. Similar behavior was observed.

The focus of future investigations will be how long the pressure has to be applied and how this could be technically realized.

The experimental work was carried out at the high pressure laboratory of the Lehrstuhl für Fluidmechanik und Prozessautomation, at the Technische Universität München. This work was supported by German Federal Ministry of Education and Research (03SF0307A).

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## POSTER: A I 11

# SUPERCRITICAL PHASE EQUILIBRIA IN TERNARY WATER-SALT SYSTEMS

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Three ternary systems ($K_2SO_4$ - KCl - $H_2O$, $K_2SO_4$ - $K_2CO_3$ - $H_2O$ and $K_2SO_4$ - $K_2HPO_4$ - $H_2O$) include one binary water-salt subsystem $K_2SO_4$ - $H_2O$ of type **2** (with critical phenomena in solid saturated solutions and supercritical fluid equilibria) and the binary subsystems (KCl - $H_2O$, $K_2CO_3$ - $H_2O$ and $K_2HPO_4$ - $H_2O$) belong to type **1** (without critical phenomena in solid saturated solutions and supercritical fluid equilibria). However, the various phase transformations were established in ternary mixtures depend on the existence of immiscibility phenomena in binary subsystem of type **1**.

The ternary systems were studied at temperatures 400-500 $^oC$ and pressures up to 100 MPa. It was found that supercritical fluid equilibria spreading from the binary subsystem of type **2** ($K_2SO_4$ - $H_2O$) were observed both below and above the temperature of binary critical end-point *Q* only in the system $K_2SO_4$ - KCl - $H_2O$, where the binary subsystem of type **1** (KCl - $H_2O$) has no liquid-liquid immiscibility. Binary subsystems of type **1** ($K_2CO_3$ - $H_2O$ and $K_2HPO_4$ - $H_2O$) are complicated by stable immiscibility region and supercritical fluid equilibria in ternary systems $K_2SO_4$ - $K_2CO_3$ - $H_2O$ and $K_2SO_4$ - $K_2HPO_4$ - $H_2O$ do not exceed the temperature of critical end-point Q in binary subsystem $K_2SO_4$ - $H_2O$.

Special studies of critical phenomena in ternary mixtures show different nature of these equilibria depend on the types of critical phenomena in binary subsystems $K_2CO_3$ - $H_2O$, $K_2HPO_4$ - $H_2O$ and KCl - $H_2O$. It was established that the monovariant critical curves of different nature started in binary nonvariant critical points *p* (G=L-S) and *Q* ($L_1$=$L_2$-S) do not intersected each other but are separated by the 4-phase immiscibility region ($L_1$-$L_2$-G-S) in the system $K_2SO_4$ - KCl - $H_2O$. At temperatures above the immiscibility region $L_1$-$L_2$-G-S there is three-phase region $L_1$-$L_2$-G that separates the isothermal critical curves $L_1$=$L_2$ and L=G, originated in binary subsystems. In ternary systems $K_2SO_4$ - $K_2CO_3$ - $H_2O$ and $K_2SO_4$ - $K_2HPO_4$ - $H_2O$, the ternary isothermal critical curves originated in binary subsystems have the same nature ($L_1$=$L_2$) and do not separated at temperatures above the critical end-point Q.

*The work was supported by the RFBR (grant 04-03-32844) and RAS (grant 9P1.17)*

# POSTER: A I 12

# THE TEMPERATURE DEPENDENCE OF THE SALTS SOLUBILITY IN AQUEOUS NONELECTROLYTE SOLUTIONS AND THEIR STRUCTURAL-KINETIC CHANGES

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The structural changes of water in the aqueous nonelectrolyte solutions (15 systems) are studied by mean of microwave dielectric spectroscopy. The complex dielectric permittivity was measured by the method of thin dielectric rod in the wave-guide at frequencies range 7-25 GHz in temperature interval 288-308 or 283-313K. The values of time and enthalpy of dielectric relaxation process are found. They reflect the changes of the molecular-kinetic mobility of water molecules in elementary hydration processes for times $10^{-11}$ s. The identical sign of time changes and different sign for activation enthalpy dielectric relaxation were established that evidence about stabilization or the disorder of the water structure in hydration processes. It is shown, what urea and glycolamide are the most strong structure-breaker, while isopropanol and dimethylurea are the most strong structure-maker of the water.

The influence of nonelectrolyte addition on the solubility diagram of $KH_2PO_4$, $KHC_8H_4O_4$, $Ba(NO_3)_2$ and $Sr(NO_3)_2$ was shown experimentally. Solubility was studied for the temperature range 298-328 K ($KH_2PO_4$ and $KHC_8H_4O_4$) and 288-343 ? ($Ba(NO_3)_2$ and $Sr(NO_3)_2$) in water and mixed solvents. The concentration of nonelectrolyte addition (urea, glycerol, acetone, isopropanol and dimethylurea) was varied up to 5-7 mol.%. The temperature solubility coefficients were calculated for all investigated salts on the basis of obtained data. It was established, what additions bringing to the stabilization of the water structure enlarge the temperature solubility coefficient. The structure-breaking additions reveal contrary action.

The theoretical scheme is given that explain the change of the temperature dependence of the salts solubility in water-nonelectrolyte systems on basis of the data on the structural change in solutions. It is possible to change the type of physic-chemical diagram when the structuredness of waters in solution is varied by the nonelectrolyte additions. As a result it is appear the methods for the directed regulation of oversaturation at growing of crystals by means of the temperature drop method.

Work is support by Russian Foundation of Fundamental Researches, grant 05-02-16825

# POSTER: A I 13

## SOLUBILITY, SPECTROSCOPIC AND VOLTAMMETRIC STUDIES ON THE BINDING OF ANTITUMOR MORIN WITH CYCLODEXTRIN AND DNA

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**Abstract:**

The phenomenon of Morin exhibiting different antitumor activities led us to consider the binding of Morin with cyclodextrin and DNA. The interaction of antitumor Morin with ß-cyclodextrin (ß-CD) and DNA has been investigated in the Britton-Robinson (BR) buffer solutions using solubility, spectroscopic and voltammetric methods. The measurements show that the Morin, acting as an intercalator, is inserted into the cavity of the ß-CD as well as into the base-stacking domain of the DNA double helix. Upon addition of ß-CD in a buffered Morin solution, the solubility of Morin increases and Gibbs free energies of transfer of the Morin aqueous solution to the cavity of ß-CD are negative and increase negatively with increasing ß-CD concentration. The binding constants were calculated from the increase of the solubility and voltammetric methods. Binding is interpreted in terms of the intercalative interactions with DNA helix or within ß-CD cavity.

# POSTER: A I 14

## THE COMPARISON OF DISSOLUTION PROCESS OF METALLIC NICKEL AND PALLADIUM IN BINARY ORGANIC MIXTURES.

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An interest in chemistry of sulfoxides is largely due to the role of their SO group as ligands, reagents and solvents. The most fundamental chemical properties of sulfoxides include their capacity for deoxygenation of sulfinyl group to give sulfide. Metal dissolution can be considered as a simultaneous action of oxidizing and complexing agents. Furthermore, it is known that with the increase in the donor number of the solvent applied, the standard potential of the metal decreases [1].

Previously we have reported on the reaction of dissolution of metallic copper in binary organic mixtures. The metallic copper can be dissolved in organic binary mixtures of DMSO and one of halogeno aliphatic derivatives. The replacement of dimethyl sulfoxide in organic mixture with different solvents did not lead to a dissolution of these metals, which confirms that the dimethyl sulfoxide was a necessary component of the dissolution process [2].

The process of dissolution of metallic nickel and palladium were carry out in binary mixtures of anhydrous dimethyl sulfoxide (DMSO) with one of the following aliphatic halogen derivatives: 1,2-dibromoethane, 1,1,2,2-tetrabromoethane, tetrabromomethane, tetrachloromethane, tribromomethane. In the succeeding stage we replaced dimethyl sulfoxide with one of the following solvents: acetonitrile, nitromethane, tetramethylene sulfone, in binary mixture.

The dissolution process of metallic nickel and palladium has been shown to occur easily in mixtures of DMSO and one of bromoaliphatic derivatives: 1,2-dibromoethane or tribromomethane, 1,1,2,2-tetrabromoethane, tetrabromomethane. Furthermore, the nickel dissolution process occurred fastest in the mixture composed of DMSO and 1,2-dibromoethane. Based on the spectroscopic analysis of the solution products in the above mixtures, the square planar palladium(II) complexes were determined. As a results of dissolution metallic nickel in binary organic system the octahedral nickel(II) complexes were obtained. As a results of differential thermal and quantitative analysis we obtained the molecular formula of complexes $Ni(DMSO)_6Br_2$ and $Ni(DMSO)_4Br_2$. The molecular formula $Pd(DMSO)_2Br_2$ of solid palladium(II) complexes as a result of quantitative analyses was assigned. The solid products is easily characterised using spectroscopic and mass spectrometry methods. The square planar coordination sphere with DMSO coordinating via sulphur atom was shown. The octahedral structures with DMSO coordinating via oxygen atom of nickel complexes were indicated.

The electrochemical study of palladium(II) complex indicated that the quasi-reversible one-electron oxidation process of Pd(II) occurred with an increase in the coordination number. The O donor and halogen ligands stabilised higher oxidation state of nickel complexes and the oxidation of Ni(II)/Ni(III) occurred easier[3].

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# POSTER: A I 15

## PIPELINE CORROSION – CARBONATE SOLUBILITY IN MIXED SOLVENT ELECTROLYTE SYSTEM

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Many pipelines in the North Sea are made from mild steel. They are 16 inches in diameter and transport on average 4 million $m^3$ natural gas/day. A breakdown will be costly. Natural gas contains small amounts of $CO_2$. Produced gas is saturated with water (wet gas) and it condenses at the cold pipe wall during transportation. NaOH and glycol (MEG) or methanol is injected to prevent gas hydrate formation and corrosion. $CO_2$ dissolves into the water-MEG-NaOH liquid phase and the electrolytic environment will corrode the lower peripheral part of the pipeline. Various protective corrosion products are produced depending on the chemical environment. $FeCO_3$ is one of the corrosion products and the corrosion rate is very dependent on its saturation index. The ionic strength in these systems is very high due to the NaOH and an activity coefficient model is needed to calculate the carbonate activity.

In this work we seek to get a better understanding of $CO_2$ corrosion in natural gas pipelines through experimental work and modelling. Only few phase equilibrium data for the $CO_2$-NaOH-$H_2O$-MEG system have been published in the open literature. Solubility measurements have been performed and the extended UNIQUAC model [1-3] is being used for modelling the system. Figure 1 shows the model performance in pure water. Result will be shown for the mixed solvent system.

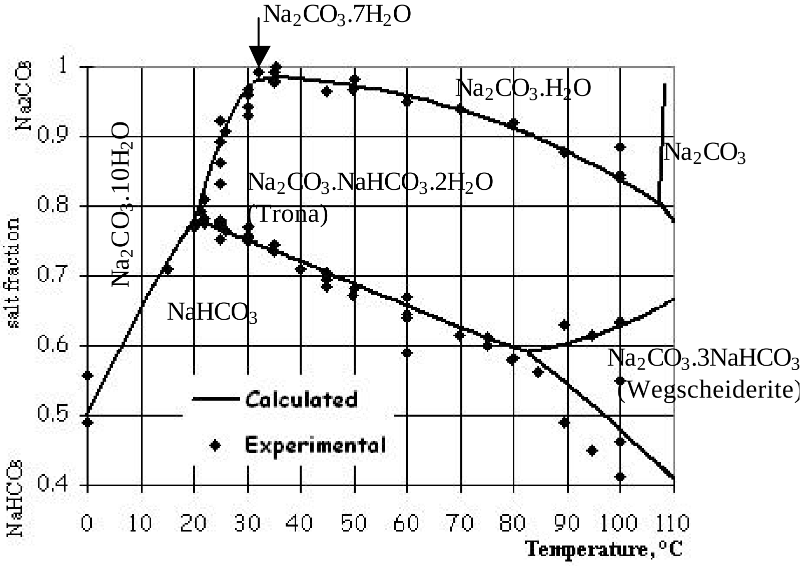

Figure 1: Phase diagram showing 2-salt lines in the ternary $NaHCO_3$-$Na_2CO_3$-$H_2O$ system as a function of temperature.

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# POSTER: A I 16

## PRODUCTION OF PU AND NP REFERENCE COMPOUNDS AS EXPERIMENTAL TOOL FOR FUTURE THERMODYNAMIC DATABASE IMPROVEMENT

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Thermodynamic solubility data are an integral component of performance assessment (PA) databases used in nuclear repository safety analysis. In order to produce reliable calculation results within PA procedures, the quality of input data needs to be assured. Many data compiled in databases are of minor quality because they are results of outdated work, unclear methodology, or just guesses. In order to realize thermodynamic data quality assurance, in some cases improvement of data by experimental support is justified or even necessary. The upcoming German project THEREDA (Thermodynamic reference database) will be concerned with aspects of thermodynamic data improvement and compilation within a critically evaluated database. The project is designed in two phases. Phase one will be dedicated to the construction of the computational frame as well as to selection and evaluation of existing data. During phase two, also (where necessary) experimental revision of thermodynamic data is planned. The German project partners are FZK-INE, FZR, GRS, and University Freiberg. JRC-ITU and Colenco Engineering (Switzerland) are associated partners.

The Institute for Transuranium Elements (ITU) is planned to support during the second phase of experimental data improvement, and to contribute with work on highly radioactive phases as reference materials. It is foreseen that ITU will particularly investigate technical radionuclide phases, such as mixed oxide nuclear fuels (solid solutions) containing changing compositions of U and Pu, metallic phases (for example Zr-alloys or metallic fission products), or certain compounds of the short-lived fission products Cs (for example Cs-uranates) and Sr (example: Sr-zirconates) which are of importance for the long-term stability behaviour of disposed nuclear fuels. Furthermore, data on certain compounds of the actinide elements Np and Pu, which were not synthesised or characterised previously as pure phases, were selected to be of importance and are planned to be investigated by ITU.

First of such compounds were investigated as part of the Actinet-6 Network of Excellence project 2-08. The phases plutonium(IV) peroxide and plutonium(IV) oxocarbonate were prepared by wet precipitation technique and characterised using scanning electron microscopy (SEM), thermogravimetry (TGA), carbonate titration and photometric analysis. Sum compositions were calculated for the solids. Pu peroxide is supposed to appear during radiolytic alteration processes and Pu oxocarbonate may appear as secondary phase during $PuO_2$ solubility processes in alkaline media. Both are so far not mentioned in thermodynamic solubility databases, although they were observed during Pu precipitation experiments. Neptunium(IV) oxocarbonate was prepared by the same technique as the Pu compound, but not yet characterised.

It was planned to continue with synthesis of further Np(IV) solids which are so far missing within databases, and to start work on plutonium(V) compounds. Possible experiments on the solubility behaviour of actinide phases were foreseen to be performed in cooperation with the ITU partners of Actinet project 2-08 (FZK-INE, FZR, NRI Rez) in a later stage of the project. In addition to the primary task of filling gaps in thermodynamic databases, such actinide reference compounds are useful for the development of a spectroscopic identification tool for spent fuel phases.

## POSTER: A I 17

# THE FACTORS DETERMINING THE ABSENCE OF DOUBLE SALTS IN TERNARY AQUEOUS CHLORIDE SYSTEMS

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In this presentation the main reasons of the absence of double salts in ternary aqueous chloride systems $MCl_x$ – $M'Cl_y$ – $H_2O$ are discussed. Based on the analysis of literature data a range of principally different systems (totally, more than 25) was chosen. For these systems solubility isotherms were studied including the gradients of components' concentrations along their crystallization branches and the hydration analysis of saturated solutions [1] was undertaken. Some systems were also investigated by vibrational spectroscopy, EXAFS technique, quantum chemistry calculations, electron absorption spectroscopy, viscometry and dilatometry. As a result of the analysis of all the data available, the next conclusions were made:

- If the cations with small ionic potential ($Ba^{2+}$, $Sr^{2+}$) are presented in the systems, their relatively week hydration and, as a sequence, high lability of water molecules in the first hydration shell is the main reason for the absence of double salts. This kind of cations is unable to form ion pairs stable enough to become the basis to form the structure of complex compound;
- Cation $Be^{2+}$ exhibits rather strong interaction between water molecules in the first and second hydration shells that is a barrier to form either non-contact or contact ion pairs. The weakening of this interaction is possible only under addition of very large amounts of alkaline chlorides. But even under these conditions the association processes are not prevailing;
- In some systems containing sodium chloride ($MgCl_2$ – NaCl – $H_2O$, $CuCl_2$ – NaCl – $H_2O$, CuCl – NaCl – $H_2O$) the absence of double chlorides is caused, from one hand, by weak influence of sodium cation on the solution structure, and, from another hand, by impossibility to reach the composition of coordination sphere of central atom corresponding to the precursors of double salts;
- The absence of complex compounds in the systems with competing complexation $MCl_2$ – $M'Cl_2$ – $H_2O$ can be due to two factors: small difference in stability constants of acido complexes (M and M' are 3d-elements) or strong distortion of coordination polyhedron of a metal as a sequence of Jahn-Teller effect of first ($Cu^{2+}$) or second ($Hg^{2+}$) type.

*Acknowledgement: Russian Foundation of Basic Research (RFBR) is thanked for the financial support (project 05-03-32099a).*

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# POSTER: A I 18

## FORMATION OF ANHYDROUS COMPOUNDS IN THE $MX_2$ – $CO(NH_2)_2$ – $H_2O$ ($M^{2+}$ = Mg, Mn, Co, Ni, Cu, Zn, Cd; $X^-$ = Cl, Br, I) SYSTEMS

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The affinity of urea to metal ions (Fig.1) leads to formation of a big variety of metal-urea complexes. In all cases of hard and intermediate in hardness Lewis acids the urea oxygen atom is bound to the metal ion, the urea $–NH_2$ groups are involved in the structures through hydrogen bonds with $X^-$ ions only.

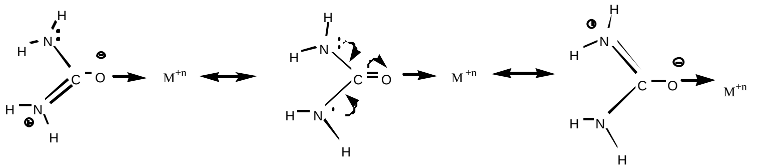

Fig. 1 Resonance structures of an urea ligand bound to $M^{+n}$ via an O-M bond.

The aim of this presentation is a survey of the known types of anhydrous compounds $MX_2.10CO(NH_2)_2$; $MX_2.6CO(NH_2)_2$; $MX_2.4CO(NH_2)_2$; $MX_2.2CO(NH_2)_2$; $MX_2.CO(NH_2)_2$ formed in the systems $MX_2$ – $CO(NH_2)_2$ – $H_2O$. The bonds in the crystal structures of these anhydrous compounds are schematically presented on Fig.2.

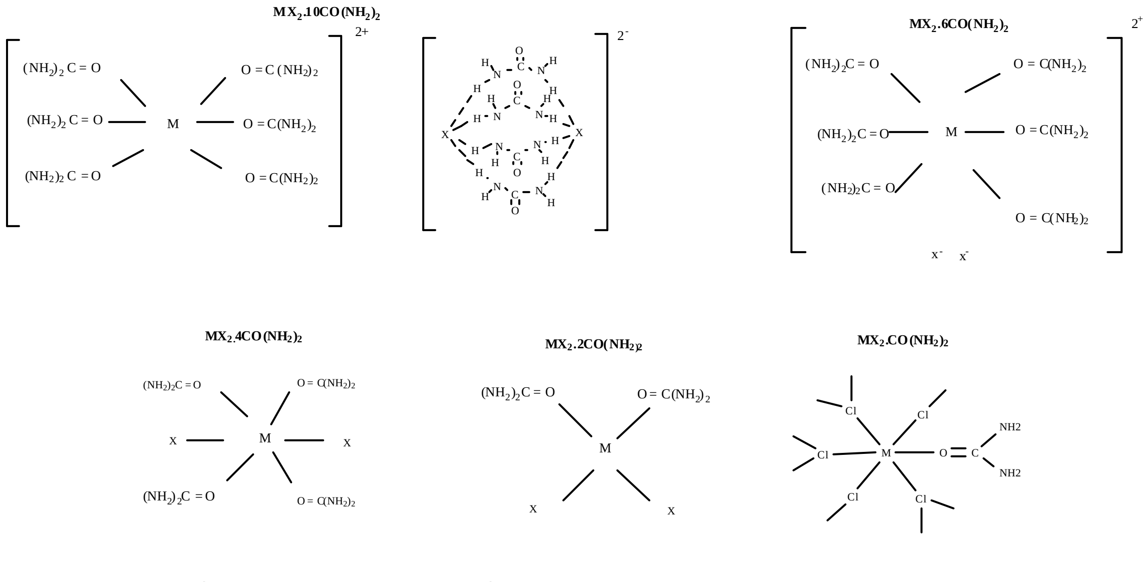

Fig. 2 Scheme of the crystal structures of $MX_2$:n$CO(NH_2)_2$ compounds (n=10, 6, 4, 2, 1).

Our studies on the system $ZnBr_2$ - $CO(NH_2)_2$ - $H_2O$ at 25°C have shown the existence of an unknown so far anhydrous compound $ZnBr_2.2CO(NH_2)_2$. It is isostructural to $ZnCl_2.2CO(NH_2)_2$, where $Zn^{2+}$ ions are in tetrahedral coordination with $2X^-$ ions and 2O atoms of two $CO(NH_2)_2$ molecules.

The interest in metal-urea compounds is based on their biological (antimicrobial and antivirial) properties, as well as on some important physical (e.g. piezo- and pyroelectric) properties. The biological importance of urea in the design of complicated molecules could be supported by the example of Vitamin B12, an inorganic coordination compound, rich in $-CONH_2$ groups.

**Acknowledgment**: The author Chr.Balarew is thankful to the Alexander von Humboldt Foundation for the 12th ISSP conference allowance.

# POSTER: A I 19

## DISSOLUTION KINETICS OF SINTERED CALCIUM PHOSPHATE IN LACTIC ACID CONTAINING SOME IONIC ADDITIVES

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Sintered calcium phosphates are widely used as bone substitutes. The investigation of the effect of various ion admixtures on the dissolution process of calcium phosphates in biologically important solutions is of interest with a view to elucidating both the physicochemical problem and some elementary processes associated with the assimilation of the biomaterials by the tissue structures.

The dissolution kinetics of sintered hydroxyapatite with 30% β-tricalcium phosphate in a buffer solution of lactic acid with pH 4.5, containing ionic additives as e.g. different amounts of zinc chloride and ammonium molybdate, at temperature (19.6ºC ±0.05º) have been investigated. A granulate (grain size~100μm) and a specific surface area of 19.0 $m^2g^{-1}$ was used for the investigations.

Obviously, the highest reaction rate is observed during the initial several minutes, after which it decreases significantly with the concentration rise of the additive in the solvent.

The ion additive adsorption on the crystalline surface at the dissolution front was interpreted theoretically using the Langmuir equation (adsorption isotherm):

$$\frac{R_0}{R_0 - R_i} = 1 + \frac{1}{K_a C_a},$$

where $R_o$ and $R_i$ are the dissolution rates in presence and absence of an inhibitor, $K_a$ is the absorption equilibrium constant, $C_a$- the impurity concentration in the solution. The process is explained by the proceeding of adsorption phenomena at the dissoluton front.

**Acknowledgements:** This work was done with the financial support of the Bulgarian Ministry of Education and Science, Project X 1509

# POSTER: A I 20

## NUMERICAL MODELING OF NATURAL BRINES IN THE SIX-COMPONENT OCEANIC SALT SYSTEM

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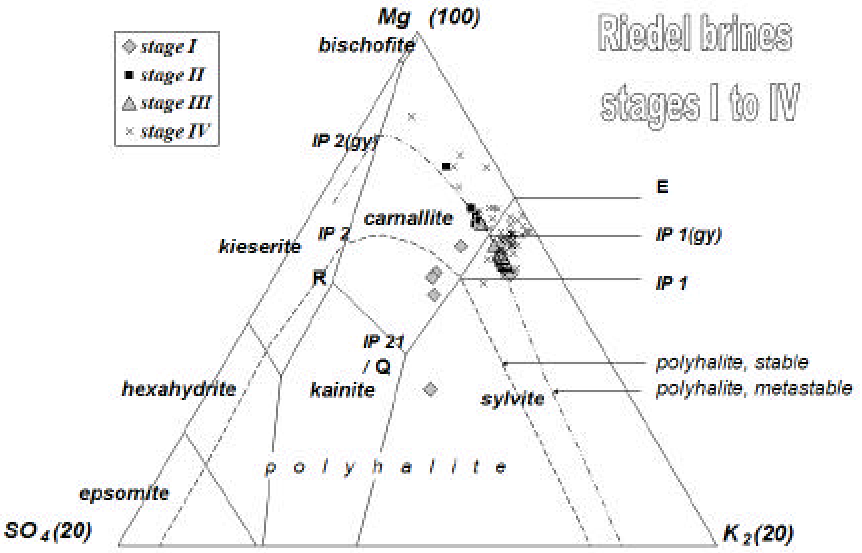
Evolution of natural magnesium chloride rich salt brines from seepages in a German potash mine was modelled [1] with the phrqpitz code [2]. The brine data reveal significant chemical changes during the 30 year period under investigation, which can be modelled by the invasion of external fluids, presumably cap rock brine, through the Stassfurt potash seam and the adjacent main anhydrite. In an initial rehydration stage, the paragenesis kieserite + anhydrite + sylvite reacted to form polyhalite + carnallite. However, temporary elimination of kieserite did not lead to a termination of the process in invariant point IP1, but instead continued to the metastable invariant point IP1(gy), with gypsum instead of anhydrite. Continued invasion of fresh cap rock brine produced univariant reactions along the carnallite-sylvite phase boundary and along the polyhalite phase boundary. Finally, elimination of polyhalite yielded solutions developing towards invariant point E of the degenerate quaternary boundary system.

The identification of the metastable processes around IP1(gy) was initially hampered by inaccurate older phase diagrams, linear approximations in more recent phase diagrams [3], lacking information on metastable equilibria, neglected Ca analyses, interference of post sampling dilution due to hygroscopic properties of concentrated magnesium chloride solutions giving misleading saturation indices, and reporting of brine analyses in terms of normalized standard salt components rather than elemental concentrations which precluded charge balance checks. These problems could be largely solved by using an internally consistent and accurate database [4] and phase diagrams based on this database for all operations, including newly calculated stable and metastable phase boundaries. Dilution effects were dealt with by plotting elemental ratios and by not using saturation indices.



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# POSTER: A II 4

## LIQUID – LIQUID EXTRACTION EQUILIBRIUM OF ZINC(II) WITH ALKYLIMIDAZOLES

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The purpose of this work was a determination of the influence of the alkyl chains on extraction of Zn(II) from aqueous solutions with alkylimidazoles. In the investigation it was used 23 derivatives from 3 homologous series of alkylimidazole, i.e. 1-alkylimidazoles (alkyl is from $C_4H_9$ up to $C_{14}H_{29}$), 1-alkyl-4(5)-methylimidazoles (alkyl is from $C_4H_9$ up to $C_{11}H_{23}$) and 1-alkyl-2-methylimidazoles (alkyl is from $C_5H_{11}$ up to $C_{12}H_{25}$). In the investigation it was used five organic solvents, namely toluene, *p*-xylene, 1,2,3,4-tetrahydronaphthalene (tetralin), 2-ethyl-1-hexanol and dichloromethane.

The values of stability constants and partition constants for all the systems were determined. It was demonstrated that both the stability constants and the partition constants of the complexes increased with increasing alkyl chain length. This referred especially to $\beta_2$ and $\beta_3$ and was due to the contribution of tetrahedral species, which enhanced the overall stability constants. The nature of the solvent was also crucial. Higher values were obtained in non-polar solvents (toluene, *p*-xylene and tetralin) as compared to the polar ones (2-ethyl-1-hexanol and dichloromethane).

The steric effect due to the presence of a 4(5)-methyl group decreased the values of stability constants of the Zn(II) complexes as compared to those with derivatives carrying a 1-alkyl group only. But in the case of 1-alkyl-2-methylimidazoles, despite stronger steric effect, the values were different than expected. It could be explained by the higher basicity of 1-alkyl-2-methylimidazoles.

The increase in hydrophobicity of ligands resulted in the increase in partition constants of the complexes. In particular, there was a considerable increase in the second and third complexation step, especially for complexes with 1-alkyl-4(5)-methylimidazoles. The steric hindrance displaced the configurational equilibrium towards the tetrahedral species, which resulted in an increase in the partition constants as compared to those obtained for the 1-alkylimidazole complexes.

As a result, the tetrahedral species formed for 1-alkyl-2-methylimidazoles and 1-alkyl-4(5)-methylimidazoles were less stable as compared to those substituted at position 1 only, but were more readily extractable with the organic solvent owing to a smaller number of co-ordinated water molecules. This creates conditions for the selective extraction of Zn(II) complexes over copper or nickel ions.

It was shown that alkylimidazoles containing from 10 to 12 methyl groups in all substituents are the most effective extractants. Further increase of the alkyl group does not improve the extraction properties of alkylimidazole. The best extraction properties showed aromatic hydrocarbons, especially tetralin and toluene. It was shown that the best extraction system are: 1-decylimidazole – *p*-xylene, 1-dodecylimidazole – toluene, 1-nonyl-4(5)-methylimidazole – *p*-xylene and 1-decyl-4(5)-methylimidazole – toluene or *p*-xylene.

# POSTER: A II 5

## STUDY ON EXTRACTIVE DESULFURIZATION OF MOTOR FUEL USING ROOM TEMPERATURE IONIC LIQUID BASED ON [BMIM]

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Room Temperature Ionic-liquids(RTILs) is a kind of liquid absolutely composed of ionic, which remains in liquid state at low temperature(<100 oC). In contrast to volatile organic extraction solvents, they have no measurable vapour pressure. There is no loss of solvent through evaporation. Environmental and safety problems arising through the use of volatile organic solvents can be avoided. RTILs have been studied for applications related to green chemical processes, such as liquid/liquid extractions, gas separations, electrochemistry, and catalysis.

Sulfur compounds present in the motor fuels lead to SOx emission to air and the pollution generated by vehicle engines. In order to minimize the negative health and environmental effects from automotive exhaust emissions, the sulfur compounds in motor fuel must be reduced to low level. RTILs have great potential solutions for sulfur–free clean fuels as extractive desulfurization solvent.

Four types of ionic-liquids: 1 -butyl -3 -methylimidazolium tetrafluoroborate([bmim]BF4), 1 -butyl -3- methylimidazolium benzothiazoy([bmim]BeS), 1-buty- 3 - methylimidazolium hexafluorophosphate ([bmim]PF6), 1-butyl-3-methylimidazolium chloroaluminate ([bmim]AlCl4) were demonstrated to be potentially applicable for sulfur removal from model motor fuel in this work. The model fuels were composed of thiophene (Thio) – n-octane, 2-Methyl thiophene (2-M-T) – n-octane, benzothiophene (BT) – n-octane, dibenzothiophene (DBT) – n-octane. The liquid-liquid equilibrium of ternary (Ionic liquid+S-containing compounds+n-Octane) were determined at 40 oC. The equlibrium of extraction was reached in 3 minutes. The distribution coefficients of Thio, 2-M-T, BT, DBT between the ionic-liquid and n-octane were measured to be 0.45, 0.28, 0.50, 0.50. The 60~90% sulfur compounds were removed from model fuel by 4 stage cross extraction with Ionic liquid/Model fuel(volume)=1:1 at 40 oC.

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# POSTER: A III 2

## INDIRECT DETERMINATION OF LOW VAPOUR PRESSURES USING SOLID-PHASE MICROEXTRACTION

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There is still a gap of reliable vapour pressure data at ambient temperature for low volatile organic substances due to the difficult and time-consuming determination using the classical methods. Static headspace extraction with a solid-phase microextraction (SPME) fibre in combination with gas chromatographic analysis provides an inexpensive tool for the indirect determination of low vapour pressures down to $10^{-5}$ Pa. The procedure consists of two steps: a) exposure of SPME fibre in the headspace above the test chemical over minutes to hours and b) desorption and quantification of extracted amount. The calibration was performed using low volatile reference substances with well-known vapour pressures. A good correlation was found between substance uptakes of SPME fibre and vapour pressures. The method was applied e.g. to tetrachlorobenzenes and to selected tetrachlorobenzyltoluenes with questionable vapour pressures. We obtained values between 0.98 and 13.5 Pa for the former and results between 0.13 and 0.68 mPa for the latter group of congeners. The scope of the method can be extended to substances with even lower vapour pressures, provided that reliable reference data are available.

# POSTER: A III 3

## A NEW SIMPLE METHOD FOR THE INVESTIGATION OF HYDROGEN SULPHIDE SOLUBILITIES IN AQUEOUS SOLUTIONS

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Compared to other natural gases only few investigations of hydrogen sulphide ($H_2S$) solubility in aqueous solutions of inorganic salts were conducted [1]. This may be attributed to the uncomfortable nature of this compound (odour, toxicity) and the complexity of experimental designs proposed so far (e.g. [2], [3]). Most of them include open flow-through systems: the gas is bubbled through the solution until equilibrium is assumed or proved by stepwise analysis of the fluid phase.

We have developed a closed system approach, where the only analytical quantity is the total gas pressure. The apparatus consists of a three-necked flask with a continuously measuring datalogging pressure sensor on top of one neck and two septa on the others (WTW Oxitop® system). First the flask is filled with a pure $H_2S$ atmosphere of unit pressure and thermostated at 25°C ± 1°C. Then a certain volume of deaerated salt solution is injected through one septum. The process of equilibration is continuously controlled by the pressure sensor, the recorded data of whom are read out via an infrared device.

Equilibrium is attained within about an hour of magnetic stirring. At constant temperature the aqueous hydrogen sulphide concentration may be derived easily from known or measured quantities like the final gas pressure, the flask volume and the solution volume. The apparatus once filled with $H_2S$ and an initial solution may be used for several consecutive measurements simply by injecting additional quantitites of water (fig. 1). We applied this new technique to investigate $H_2S$ solubilities in concentrated solutions of NaCl, KCl, $MgCl_2$, $Na_2SO_4$, $K_2SO_4$ and $MgSO_4$.

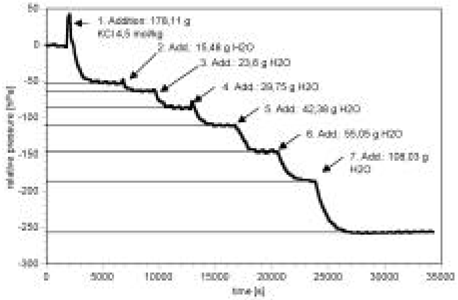

Fig. 1: $H_2S$ pressure above KCl

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# POSTER: A III 4

## ACTIVITY IN ME-S SYSTEMS BY SOLID-STATE GALVANIC CELL TECHNIQUE

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The phase relations between pyrrhotite and pyrite can be described by the solid-phase reaction:

$$FeS_2(cr) + 2Ag(cr) = \text{‘FeS’}(cr) + Ag_2S(cr)$$

where pyrrhotite is solid solution of FeS and $V_{Fe}S_S$ ($a_{FeS}<1$).

The reaction was studied by measuring the temperature dependence of the electromotive force (EMF) of the all-solid-state galvanic cell with common gas space:

$$(-)\ Pt\ |\ Ag\ |\ AgI\ |\ Ag_2S,\ \text{‘FeS’},\ FeS_2\ |\ Pt\ (+)$$

The cell can be presented as a combination of two half-cells and pyrrhotite – pyrite equilibrium, which serves as a sulfur source (solid-state buffer):

*Left half-cell:* $2Ag(cr) = 2Ag^+ + 2e$

*Right half-cell:* $2Ag^+ + 2e + 0.5S_2(g) = Ag_2S(cr)$

$FeS_2(cr) = \text{‘FeS’}(cr) + 0.5S_2(g)$

*Net potential-forming process:* $FeS_2(cr) + 2Ag(cr) = \text{‘FeS’}(cr) + Ag_2S(cr)$

In this case, the pyrrhotite compositions in equilibrium with pyrite need not be known.

The equilibrium in the cell was attained quickly (<48 hours) and reproducibly over the whole temperature range studied. The relatively high mobility of silver ions and electronic conductivity resulted in the quick establishment of equilibrium between the solid phases of the sample system.

Data obtained from the EMF measurements described by two linear ($?_r?_p = 0$) equations, which refer to the fields of equilibrium of pyrite with high-temperature (?) and low-temperature (ß) pyrrhotite, respectively:

$E(?+py)$, mV = $-(311.7 \pm 1.1) + (0.5968 \pm 0.0017)\cdot T$, $(601<T/K<723)$, $R^2=0.9999$

$E(ß+py)$, mV = $-(290.9 \pm 1.4) + (0.5621 \pm 0.0025)\cdot T$, $(518<T/K<601)$, $R^2=0.9998$

$T_{trs}=(601 \pm 2)K$, $?_{trs}H=(4020 \pm 200)$ J.mol$^{-1}$

The temperature dependence of the gaseous sulfur activity above the pyrrhotite-pyrite equilibrium can be determined by substitution of equations $E(T)$ into equation,

$\log aS_2 = (-9174.5 + 20.159\cdot E/\text{mV})\cdot T^{-1} + 3.61$,

(which was obtained by only Gibbs energy of $Ag_2S$ formation from Ag and $S_2(g)$[1]):

$\log aS_2(?+py) = (15.64 \pm 0.035) - (15455 \pm 23)\cdot T^{-1}$, $(601<T/K<723)$

$\log aS_2(ß+py) = (14.95 \pm 0.05) - (15040 \pm 28)\cdot T^{-1}$, $(518<T/K<601)$

Thus, determination of the gaseous sulfur activity in Me-S systems is possible by solid-state galvanic cell technique with common gas space in addition to the electrum-tarnish method [2] and potentiometric gas sensor [3] provided that contents of silver in Me-S system and Me in argentite do not exceed 1 at.%.

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# POSTER: A III 5

## ISOTHERMAL HYDRATION HEAT OF $MGSO_4$ HYDRATES AT VARIOUS HUMIDITY

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The storage of low-temperature solar heat is a fundamental way for saving fossil fuels. The principle for energy storage by the utilisation of the hydration of salts is the reversible reaction of a desorbed salt hydrate with water vapour by releasing heat.

The aim of this work is to discuss the differences between the heat of hydration above and below the deliquescence relative humidity (DRH) for $MgSO_4$ hydrates. The DRH of epsomite ($MgSO_4 \cdot 7\ H_2O$) is about 90 % RH and the kind of the hydration product solid salt hydrate or salt solution depends on the partial water vapour pressure at the environment of the crystals (corresponding to Eq. 1 and 2, Fig. 1).

salt(s) + water (g) ? salt hydrate (s) for RH < DRH (1)
salt(s) + water (g) ? salt solution (l) for RH > DRH (2)

The device for measuring the isothermal heat of hydration at 30 °C was a calvet-calorimeter (C 80, Setaram) connected with a humidity controller (WETSYS, Setaram). Starting substances were a magnesium sulphate, dried at 130 °C ($MgSO_4 \cdot 1{,}3\ H_2O$) and starkeyite ($MgSO_4 \cdot 4\ H_2O$). It is expected, that the maximum final states after the hydration will be epsomite crystals below the DRH and an aqueous solution of $MgSO_4$, above.

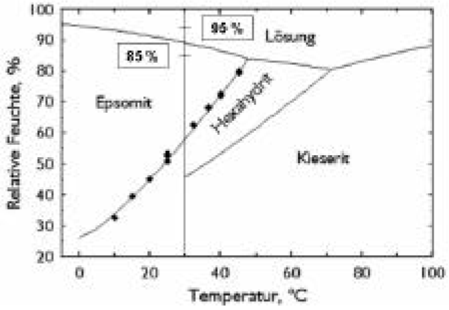

Fig. 1 : Diagram of $MgSO_4$ hydrates [1] with parameters of measuring

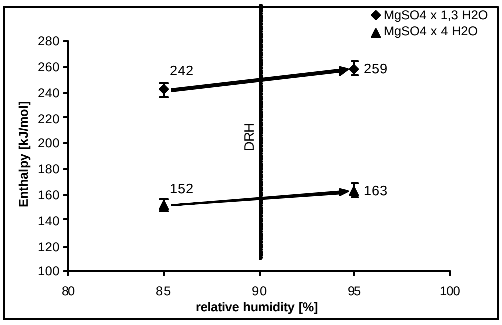

Fig. 2: Measured hydration enthalpies above and below the DRH of $MgSO_4 \cdot 7\ H_2O$

The measured heats of hydration (Fig. 2) of the solid-gas reaction at 95 % RH (see Eq. 2) are notable higher than those at 85 % RH (see Eq. 1). The enthalpies, calculated from the enthalpies of formation [2], for the reactions from $MgSO_4 \cdot 1{,}3\ H_2O$ ($MgSO_4 \cdot 4\ H_2O$) to epsomite are -321 kJ/mol (-170 kJ/mol) and to hexahydrite -260 kJ/mol (-108 kJ/mol). The measured hydration enthalpy below the DRH of $MgSO_4 \cdot 1{,}3\ H_2O$ (242 kJ/mol) corresponds approximately with the calculate value for the hydration to $MgSO_4 \cdot 6\ H_2O$ and the hydration of starkeyite (152 kJ/mol) with the value of formation of epsomite. Both results were corroborated by the contents of water of the formed minerals.

In consideration of observed crystals after the hydration above the DRH, the increased enthalpies will be discussed by the simultaneous effect of exothermic heat of condensation and endothermic heat of solution in connection with the formation of a solution film on the surface of the crystals.

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# POSTER: A IV 1

## TEMPERATURE DEPENDENCE OF OCTANOL/WATER PARTITIONING OF HEXACHLOROCYCLOHEXANE ISOMERS

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The octanol/water partition coefficient ($K_{ow}$) is one of the key parameters for modelling the environmental fate of persistent organic chemicals. $K_{ow}$ values are usually determined at ambient temperature but for quantifying phase distribution at temperatures others than 20-25 °C knowledge of its temperature dependence is necessary. We determined the $K_{ow}$ of α–, β–, γ–, and δ–hexachlorocyclohexane (HCH) between 5 and 45 °C using the slow-stirring method followed by solid-phase microextraction (SPME) fibre in combination with gas chromatographic analysis. The variation of $K_{ow}$ is greater between 5 and 25 °C than from 25 to 45 °C. Van't Hoff plots yield values for the enthalpy and the entropy of phase transfer and allow further thermodynamic interpretation of the partitioning process of HCH isomers between water and octanol.

# POSTER: A IV 2

## AIR-WATER PARTIONING OF SELECTED ORGANIC COMPOUNDS AT AMBIENT TEMPERATURE

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Henry's law constant (HLC) is one of the key parameters for estimating the environmental fate of waterborne organic micropollutants. For a group of organic compounds (detected e.g. in groundwater of the Bitterfeld region) where reliable experimental data are scarce, two different methods were employed to determine HLC values at 298 K experimentally: The EPICS (EPICS = equilibrium partitioning in closed systems) method and the PRV (PRV = Phase ratio variation) method, both in combination with solid-phase microextraction (SPME) and GC-MS analysis. The compound set includes chlorinated anilines and toluenes. The results are compared with predicted values using established estimation methods, and discussed with respect to differences in the experimental performance of the two methods employed.

# POSTER: A IV 3

## PARTITION COEFFICIENTS OF PHARMACEUTICALS BETWEEN WATER AND SILICONE ELASTOMER

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Silicone elastomer (in flexible rod form) is one of the materials that are currently tested for use in analytical extraction techniques and passive sampling devices. In the present investigation, we focus on the performance of silicone rod for waterborne polar pharmaceuticals, and compare their enrichment characteristics with the ones of chlorinated hydrocarbons and polycyclic aromatics. Uptake and elimination kinetics as well as equilibrium distribution constants were determined, employing both long-term batch equilibrium tests and kinetic tests according to OECD guidelines. Liquid chromatography coupled with mass spectrometry was applied for the chemical analysis. The discussion includes a comparison of the equilibrium distribution constants obtained from the two approaches, and their correlation with the octanol/water partition coefficients.

# POSTER: A IV 4

## MEMBRANE-WATER PARTITIONING OF ORGANIC COMPOUNDS – EVALUATION OF DIRECT MEASUREMENT METHODS

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Literature data on ionogenic compounds indicate that the octanol/water partition coefficient $K_{\mathrm{ow}}$ does not properly mimic their uptake into biological materials. Here, the membrane/water partition coefficient $K_{\mathrm{mw}}$ has proven useful to quantify the bioconcentration into lipid compartments from ambient water. In the present investigation, we focus on experimental limitations in terms of the hydrophobicity range available for currently used direct $K_{\mathrm{mw}}$ measurements that employ liposomes as model membranes. Using both equilibration dialysis and solid phase microextraction (SPME), $K_{\mathrm{mw}}$ investigations include alcohols and aromatics, and the results are discussed in view of derived measurement limitations associated with the experimental settings.

# POSTER: A V 1

## INVESTIGATION OF ELECTROLYTE SOLUTIONS CHLORIDE, SULFATE, NITRATE AND PHOSPHATE USING THE HYGROMETRIC METHOD.

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The behaviour of aqueous electrolyte solutions is of great importance in areas such as chemical[1-3], process engineering [4-6], biological [7], desalination [8], and process atmospheric[9,10]. Free energy values species distribution, water activity, activity and osmotic coefficients, are of fundamental importance to understand and predict behaviour in aqueous electrolyte systems. In order to facilitate the use of mixed electrolytes, in these processes, it is desirable to know accurately the thermodynamic parameters in the mixture.

Thermodynamic properties for these solutions have been investigated at temperature 298.15 K using the hygrometric method. These studies concern binary and ternary of aqueous electrolyte solutions of chlorides, sulfates, nitrates [11-14] and phosphates.
Measurements of water activities were made for total molality range from 0.1mol.kg$^{-1}$ to saturation at 298.15 K. The osmotic coefficients are evaluated for the solution from the water activities. The experimental data are used to calculate activity coefficients of solute, using the ion interaction model of Pitzer [15] and excess Gibbs energy is detemined.

### Experimental method

We have employed the hygrometric method, which is based on the measurements of the relative humidity above the solutions containing non-volatile electrolytes. The relative humidity of a salt solution is identified particular with the water activity of this solution.

The experimental apparatus and procedures are described in our previous work[11]basically they consists of the following parts: a thermostatted box formed by a chest freezer, a wood box, a contact thermometer, a heat circuit, two fans, and an electronic relay. The fluctuations of temperature inside the wood box, which is in thermal equilibrium with the freezer box are less than ±0.02 K. The droplet diameter is measured by a microscope with an ocular equipped with a micrometric screw.

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# POSTER: A V 2

## POTENTIOMETRIC STUDY OF THE STABILITY CONSTANTS OF CADMIUM CHLORIDE COMPLEXES FROM 1 TO 1000 BAR AT 25°C

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Potentiometric measurements have been performed using an isothermal cell with liquid junction. A solid contact Cd-selective electrode (“Niko-analit”) and a specially designed reference electrode [1] were used. Measurements were performed in solutions of constant $Cd(NO_3)_2$ concentration (0.01*m*) and variable concentration of KCl (0, 0.025, 0.53 and 1.4*m*) at 25°C and pressure from 1 to 1000 bars.

The electrodes were calibrated using $Cd(NO_3)_2$ solutions at pressures of 1-1000 bars and 25°C. At all pressures, the calibration data (*E*, vs. pCd) define a straight line with a near theoretical Nernstian slope ($30\pm0.5$mV/pCd). $E^o$ decreases by $10\pm0.5$mV with a pressure increase from 1 to 1000 bar (fig.).

In order to verify the electrode system, a 0.01m $Cd(NO_3)_2$ solution was first titrated with a KCl solution and cadmium chloride stability constants ($ß_1$, $ß_2$, $ß_3$, $ß_4$) were determined. The obtained values of stability constants are in a good agreement with previous estimates.

The values of partial molar volumes of cadmium chloride complexes and the HKF parameters ($a_1$ - $a_4$) were determined: $V^o$ ($CdCl^+$) = 8.11, $V^o$ ($CdCl_{2\ aq}$) = 31.88, $V^o$ ($CdCl_3^-$) = 50.52, $V^o$ ($CdCl_4^{2-}$) = 98.58 $cm^{-1}$ $mol^{-1}$. All the stability constants of cadmium chloride complexes show very weak pressure dependencies – lg $ß_q$ decreases by 0.06-0.13 as pressure rises from 1 to 1000 bar.

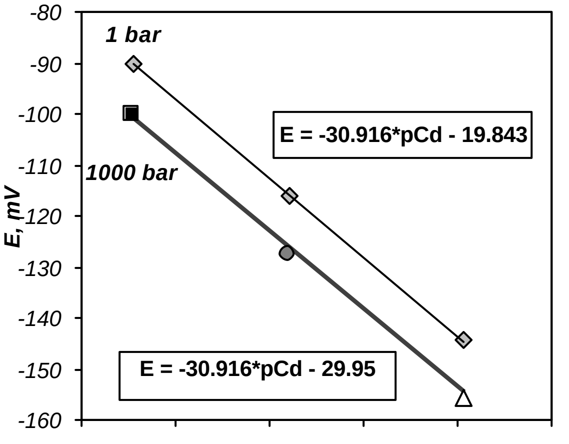

Fig. Calibration curves for the Cd-selective electrode from 1 to 1000 bar at 25°C.

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## POSTER: A V 3

# NON-ADDITIVITY OF CONTRIBUTIONS INTO THE DIELECTRIC CONSTANT OF SATURATED SOLUTIONS AND ION-ION INTERACTIONS IN TERNARY WATER-SALT SYSTEMS

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The hydration interactions alongside with ion-ion ones concern to the basic characteristics determining physico-chemical properties and equlibria in solutions. The hydration in most cases can not be determined directly. The method of the microwave dielectric spectroscopy allows to receive simultaneously physico-chemical parameters of solutions describing as molecular-kinetic state of solvent (by means of a dielectric relaxation time) and hydration interactions in electrolyte solutions (by means of static dielectric constant which determines electrostatic interactions in solutions).

Hydration and complexation were investigated in saturated solutions of model ternary water-salt systems by methods of microwave dielectric and electronic spectroscopy. The interrelation between character hydration, ion-ion interaction in solutions and the type of solubility isotherms in multicomponent water-salt systems is revealed. The method of analysis of non-additivity of contributions in $\varepsilon_s$ from the data for binary systems is offered for studies of association and complexation in the saturated and nonsaturated solutions of ternary water-salt systems. It concludes the determination of the difference between experimental ($\varepsilon_s^{exp}$) and calculated ($\varepsilon_s^{add}$) values of dielectric constant. The decrement of the dielectric constant $\Delta\varepsilon_S$, caused by addition of each component at constant amount of water calculated as: $\Delta\varepsilon_S = \Delta\varepsilon_S^{salt\ I} + \Delta\varepsilon_S^{salt\ II}$ , where $\Delta\varepsilon_S^{salt\ I}$ and $\Delta\varepsilon_S^{salt\ II}$ - decrement of $\varepsilon_s$ in binary solutions at appropriate molal concentration of salts in ternary system. The additive values of $\varepsilon_s$ are equal: $\varepsilon_S^{add} = \varepsilon_S^{water} - \Delta\varepsilon_S$

The concentration curves of $\varepsilon_S^{add}$ and $\varepsilon_S^{exp}$ in the saturated solutions of ternary systems have a similar kind. However the distinction in experimental and calculated values of dielectric constant is observed. The maximal distinctions of these values correspond to special points on phase diagram. It is explained by the association of ions and liberation of water molecules from the coordination spheres cations. This processes lead to increase of part of less "frozen" water and accordingly to growth of $\varepsilon_s$ values. Therefore positive values of $\Delta\varepsilon_S$ testify to presence more expressed ion-ion interactions in solutions of ternary system in comparison with binary solutions with the same concentration of water. The presence of complexation and association was confirmed by the electronic spectroscopy in the solutions model systems containing different salts ($Cu(CHOO)_2$, ect.).

Thus, the analysis of non-additive contributions in $\varepsilon_s$ for ternary systems can be used to allocate presence of ion-ion interactions, especially in case when other experimental methods are not informative. The microwave dielectric spectroscopy appears an effective method for research of the saturated salt solutions and phase equilibria. The analysis of dielectric properties of the saturated solutions allows to predict a type of solubility diagrams.

*This work was supported by the grants of Presidium of RAS*

# POSTER: A V 7

## TIN(IV) CHLORIDE ADDUCTS OF PHOSPHINE OXIDES : A MULTINUCLEAR ($^{119}$Sn, $^{31}$P, $^{19}$F and $^{1}$H) NMR CHARACTERISATION IN SOLUTION

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Studies of tin(IV) adducts continue to provide fundamental information about both the Lewis acid-base model and the reactivity of tin species [1,2]. In a previous work, we have shown that the stereochemistry of the octahedral complexes $SnCl_4.2(Me_2N)_2P(O)F$ [3] (**1**) and $SnCl_4.2Me_2NP(O)F_2$ [4] (**2**) depended on the basicity of the ligand used.. Here we report the characterisation of these complexes using multinuclear ($^{119}$Sn, $^{31}$P, $^{19}$F and $^{1}$H) NMR spectroscopy in solvents of different polarities. The NMR spectra in dichloromethane solution showed at slow exchange that complex **1** exists as a mixture of cis and trans isomers 80 % and 20 % respectively, whereas in chloroform complex **1** showed the existence of nearly only the cis isomer. The assignment was further confirmed by the $^{2}J_{119Sn-31P}$ and $^{1}J_{P-F}$ coupling constant values. The effects of changing the solvent polarity on the stereochemistry of the complex formed will be discussed.

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[4] Results to be published.

# POSTER: A V 9

## SOLUTION ENTHALPIES OF ORGANIC SOLUTES IN THE IONIC LIQUIDS BUTYL-TRIMETHYL-AMMONIUM (TRIFLUOROMETHYLSULFONYL)IMIDE AND 1-ETHYL-3-METHYL-IMIDAZOLIUM ETHYL-SULFATE

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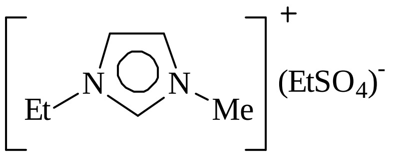
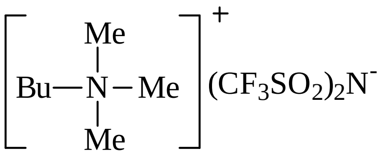
All currently published research results indicate that the unique character of ionic liquids offers new opportunities in catalysis and organic synthesis. Some of the properties that make the room temperature ionic liquids (IL) attractive for various applications are the wide liquid range, non-volatility, their non-flammable nature, and the ability to dissolve a large variety of organic and inorganic substances. In continuation of our intensive work on thermodynamic properties of IL and mixtures containing ionic liquids we present new data of the heats of solution of 8 ionic liquid+solute systems with the ILs:



1-Ethyl-3-methyl-imidazolium
ethyl-sulfate



$[\mathrm{Bu{-}N(Me)_3}]^+ (CF_3SO_2)_2N^-$

*Butyl-trimethyl-ammonium*
*bis(trifluoromethyl-sulfonyl) imide*

The heats of solutions of the different solvents in IL were measured in the mole fraction range 1% - 14% of the solute at 25 $^0$C using a titration calorimeter (Thermal Activity Monitor 2277) equipped with a 4-ml titration cell. The solutes were injected using a Hamilton Microlab M motor driven pump with a 100 mm$^3$ syringe in steps of 5 to 10 mm$^3$ into the cell containing about 4 g of the ionic liquid.

The heat effect of solute injection into the IL was transformed in the molar enthalpy of solution by the formula:

$$H_i^E = \left(\frac{\partial H^E}{\partial n_i}\right)_{T,p,n_{IL}} \approx -\frac{Q_i}{\Delta n_i}$$

where ? $n_i$ (given in moles) denote the amount of solute added stepwise to the ionic liquid in the solution, $H^E$ is the excess enthalpy of mixing and $Q_i$ is the heat observed per injected drop.

For all investigated solvents the dependences of the partial enthalpy of solution on the mole fraction of solute have been determined, and the limiting partial molar excess enthalpy ( $H^{E\infty}$ ) have been obtained by extrapolation to infinite dilution.

A comparison of $H^{E\infty}$ of the solutes in ionic liquids measured by calorimetric titration method and those calculated from temperature dependence of limiting activity coefficients obtained by GLC method are presented.

# POSTER: A V 10

## THE THERMOCHEMIC APPROACH FOR AN ESTIMATION FEATURES OF SOLUTION AND SOLVATION PROSESSES THE SINSETIC PORPHYRINS IN ORGANIC SOLVENTS ON THE EXAMPLE OF TETRAKIS(3,5-DI-T-BUTYLPHENYL)PORPHIRINATS

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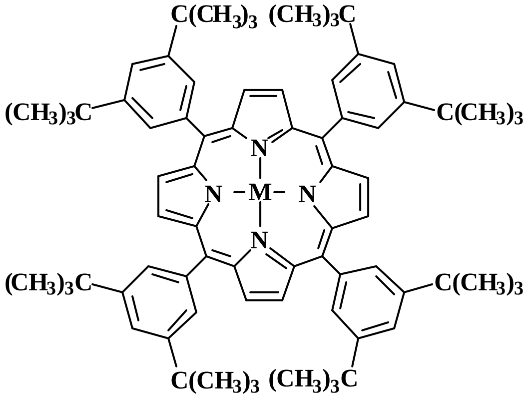
For understanding a mechanism of the interaction of porphyrins with a bio-environment the set of modeling synthetic systems containing compounds of the given class have been investigated by various methods. In the given work we have chosen as modeling system the metallocomplexes of tetrakis(3,5-di-*t*-butylphenyl)porphin in a solvate environment of organic molecules solvent (cyclohexane, benzene, chloroform, pyridine). Such choice of solvents have been allowed to capture the all most characteristic types of interactions for "? ? - molecular ligand" systems, and to allocate the power contribution of a specific solvation into reorganization structure process of a solvent and a dissolved substance by means of a comparative analysis of the enthalpic characteristics obtained for a dissolution process of modeling object.



tetrakis(3,5-di-*t*-butyl-phenyl) porphyrinat (MÐ)

With this purpose the processes of dissolution and transfer of ? ? in the specified organic solvents have been researched by a calorimetric method at 295.15. The enthalpy dissolution values are received and transfer enthalpies from benzene and axial coordination of pyridine on ? ? are calculated.

It is known, that the basic problem at studying features of solvation interactions of porphyrin is an absence of the data on sublimations enthalpies. Therefore it was offered to use the transfer enthalpy, calculated as a difference of dissolution enthalpies of ligand in researched and "standard" solvents. However such approach assumes the absence of specific interactions in system the porphyrin – "standard" solvent. The choice of "standard" (it is benzene more often) is not always correct, as is limited an enough to low solubility of synthetic porphyrins in organic solvents. Ours objects possess the increased solubility and are dissolved even in cyclohexane. It has allowed to reveal and for the first time to estimate the specific p - p interactions of benzene with ? ?.

## POSTER: A V 11

# FROM SOLUTION EQUILIBRIA AND EQUILIBRIA IN SOLUTIONS TO GAS-SOLID PHASE INCLUSION THERMODYNAMICS

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Molecular recognition of vaporous guests by the solid hosts is of great interest in many research and engineering areas. Encapsulation of gases by cavity-containing solid materials is crucial for developing new gas separators, sensors and storage devices for use in fuel-cells. The design of novel syntetic cavities for gas inclusion is a quickly emerging research area. Clathrates, cross-linked polymers, carbon nanotubes, dendrimers, calixarens, fullerens and cyclodextrins were proposed as suitable molecular containers for gases of different nature [1,2]. Nevertheless, the driving forces of inclusion in heterogeneous systems are much less studied as comparing with that in pure condensed (liquid, solid) or gas phase.

In the present work, the complex formation of different primary, secondary and tertiary amines by ß-cyclodextrin is studied. The reactions in water and at the gas-solid interface are related with the Gibbs free energies and enthalpies of solution of the reaction participants (solid cyclodextrin, gaseous amine and “solid-gas” complex) via a thermodynamic cycle. Free energies of solution of the complexes in water determined from solubility measurements appear to be nearly identical with that of β-cyclodextrin. It makes possible thermodynamic parameters for the reactions between solid ß-cyclodextrin and several gaseous amines to be determined using the data obtained in aqueous solution. Stability constants are comparable with the corresponding data in aqueous solution due to enthalpy-entropy compensation. Unlike the equilibria in aqueous solution, the reaction enthalpies for the “solid-gas” complexation are much higher and the interactions are unfavorable in terms of the entropy changes. A more detailed description is obtained from the analysis of electrostatic and covalent contributions to thermodynamic parameters of transfer for complexation reactions [3]. The electrostatic contributions to enthalpies of transfer from the gas-solid conditions to aqueous solution are unfavorable (positive) and increase with the number of methylene groups in the alkyl chains of the amines. Covalent contributions are negligible. Water in this special case displays itself only as a medium for electrostatic interactions.

Studies related to complexation thermodynamics of other macrocycles with different gaseous organic and inorganic substances are underway.

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# POSTER: A V 12

## DIFFUSION PHENOMENA IN THE SYSTEM SULFURIC ACID-WATER: APPLICATION TO THE EXTREME ENVIRONMENT OF TINTO RIVER, SPAIN

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The importance of Tinto River (Huelva, Spain) acidic environment as a terrestrial analogue for search of past or present life on Mars is now widely recognised. The study of its water has thus become crucial to understand the life in the Red Planet.

The red colour of the water and the average pH 2 [1] (highly acidic) are due to the natural abundance of iron sulphates. Recent investigations [2] show that certain bacteria that live in the river turn these sulphates into sulfuric acid, providing the river such low pH. Other bacteria oxidize the iron, giving the river its characteristic red colour.

Physical-chemical characterization of the river acidic aqueous is of great importance in the understanding of the biogenic processes in Tinto ecosystem.

In the present study the diffusion of molecular species of the system sulfuric acid-water inside vertical tubes with suppressed convection is monitored by Raman spectroscopy. A physical-chemical model taking account of equilibrium and diffusion phenomena of the species in solution is proposed and the diffusion coefficient of sulfuric acid is calculated –for the first time at our knowledge– by using Raman spectroscopic techniques.

As a non-invasive technique, Raman spectroscopy has shown to be a very powerful tool that allows an accurate quantitative analysis of the concentration of the species present in the mentioned system (Figure 1) and the potential applications of Raman spectroscopy for *in-situ* analysis of Tinto River geochemistry and analogous extreme environment conditions with Astrobiological implications are proved. In this context, a Raman spectral study of the also extreme hydrogeochemistry of Iron Mountain Superfund Site, California is expected to be performed by summer of 2006.

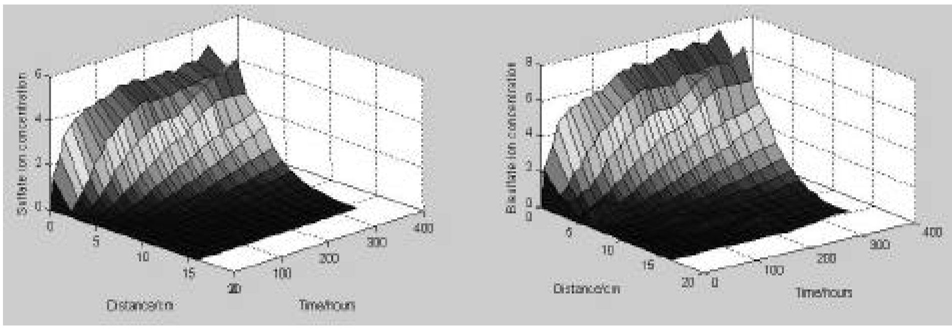

Fig. 1: Raman spectroscopy is used to calculate ions concentration as they diffuse along a vertical tube

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# POSTER: A V 13

## THERMODYNAMICS OF INTERMOLECULAR INTERACTIONS IN SALTS AND SOLUTIONS OF LINEAR TETRAPYRROLES

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The present research was directed on studying of correlations structure – physical and chemical property for salts of linear tetrapyrroles.

In the report thermodynamic stability characteristics of dihydrobromides of alkyl – substituted of biladien-*a,c* in various phase states are analyzed depending on a structure of a heterocyclic ligand, a nature of environment and temperature.

For an estimation of thermal stability of salts of linear oligopyrroles correlation ratio between parameter of basicity (proton affinity) of ligands and enthalpies of evaporation of hydrogen bromide from their crystal salts, designed of the data of computer modelling and a thermogravimetric analysis, accordingly are offered.

Other direction of researches was connected to studying power characteristics and features of salvation of bilirubin and its synthetic analogues in various organic solvents on a nature [1]. As synthetic models of bilirubin alkyl – substituted of biladien-*a,c*: 1,2,3,7,8,12,13,17,18,19-decamethylbiladien-*a,c* and 1,3,7,8,12,13,17,19-octamethyl-2,18-diethylbiladien-*a,c* as salts with the hydrobromide acid acting as stabilizing agent, preserving compounds from oxidation by molecular oxygen of air are chosen. The variation of a nature of organic solvents has allowed to study modeling systems with various types of universal and specific interactions solute - solvent.

The analysis of the data on $\Delta_{sol}?^0$ has shown, that non-polar solvents ($?_6?_6$ and $??l_4$) show the lowest solvating ability in relation with bilirubin and dihydrobromides of alkyl – substituted of biladien-*a,c*, that has allowed to assume benzene for "standard" solvent at calculation of enthalpies of conduction ($?_{tr}?^0$). The highest negative values $?_{tr}?^0$ characterize processes of conduction of compounds to electron-donating solvents ($??_3$CN, D? F, D? SO and $C_5H_5N$). Results of the spectrophotometric control testify that at dissolution of salts of biladien-*a,c* in electron-donating solvents processes of irreversible deprotonation of ligands owing to specific salvation of a proton of hydrobromide by electron-donating molecules of solvent proceed. It is shown, that for salts of synthetic biladiens-*a,c*, sizes $?_{tr}?^0$ well correlate with values of donor numbers on Gutman.

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# POSTER: B 1

## SOLID PHASE FORMATION IN TERNARY AQUEOUS SYSTEMS WITH COMPETING COMPLEXATION

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The problem of chemical interactions in concentrated solutions and their effect on solid phase formation is of great interest and actuality. A great deal of systems has been studied, with hydration, complexation, ionic association and hydrolysis being dominating processes. However systems containing two cations as complexing agents and common anion as acidoligand, *i. e.* systems with competing acidocomplexation, are little studied. This presentation is devoted to the analysis of solid phase formation in the systems of this kind.

The study of a wide range of solubility isotherms in $MCl_2 – M'Cl_2 – H_2O$ systems has shown that the form of the $MCl_2{\cdot}nH_2O$ crystallization branch in such systems is determined mostly by the competition of following processes:

$$MCl^+ + Cl^- \ ?\ MCl_2 \qquad (1)$$

$$MCl_2 + nCl^- \ ?\ MCl_{n+2}{}^{n-} \qquad (2)$$

$$MCl_a{}^{2-a} + M'Cl_b{}^{2-b} \ ?\ MCl_c{}^{2-c} + M'Cl_d{}^{2-d} \qquad (3)$$

Increase in the neutral complex ($MCl_2$) concentration would lower the solubility of a corresponding salt, and *vice versa*; so the reaction (1) results in salting-out process, while the reaction (2) gives rise to salting-in. The competition of two complexing agents that may be described by the reaction (3) leads to the growing of salting-out field and attenuation of salting-in process.

The competing complexation also affects substantially double salt formation. The analysis shows that the possibility of formation as well as the composition and structure of such salts are determined to a large extent by the stability constants of acidocomplexes of both metals.

In the case of similar values of stability constants double salt formation doesn't occur (*e. g.*, $ZnCl_2 – CuCl_2 – H_2O$, $CuCl_2 – NiCl_2 – H_2O$ systems), and only if the cations radii are nearly equal the solid solution formation is possible (*e. g.*, $CoCl_2 – NiCl_2 – H_2O$).

If the difference in stability constants is high enough double salts consisting of discrete aquacations and complex anions crystallize *(e. g.*, $[Ni(H_2O)_6]_2[CdCl_6]$, $[Co(H_2O)_6][CdCl_5(H_2O)]_2$).

If the stability constants of both complexes are sufficiently large and differ one from another not essentially (1 – 2 orders of magnitude) the solid heteronuclear complexes can crystallize ($CuCdCl_4{*}4H_2O$). The metal ions environment in such salts correlates with corresponding stability constants.

However this correlation can fail if the crystallographic parameters for the possible compound are unfavorable for the formation of three-dimensional structure. Then either salts with unexpected structure ($CoHgCl_4{*}4H_2O$ salt with $[Co(H_2O)_4Cl_2][HgCl_2]$ rather than $[Co(H_2O)_4][HgCl_4]$ structure), or no double salt ($CuCl_2 – HgCl_2 – H_2O$ system) can be formed.

Acknowledgement: RFBR (project 05-03-32099a) is thanked for the financial support.

# POSTER: B 3

## A METHOD OF RECONSTRUCTION OF ENTIRE PHASE DIAGRAM OF AQUEOUS SOLID-SOLUTION SYSTEMS

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The main problem of the investigation of phase diagrams of water-salt systems under the formation of solid solutions is to determine equilibrium solid phase composition. There are two factors produce this problem. First, solid phase practically cannot be separated entirely from liquid one. Correspondingly, composition of a solid phase is determined by an extrapolation procedure (for example, by Schreinemakers method), which seriously decreases precision. Second, only surface layer of solid solution is in the equilibrium with liquid phase, while the deep part of crystals can be of arbitrarily different composition. The composition obtained by chemical analysis generally is the bulk composition of solid solution.

Nevertheless, one can suggest a method by which the whole information about the mentioned system can be obtained on the basis of liquid phase composition data exclusively. Let us consider ternary system formed by two soluble components, S1 and S2, and solvent, W, under isothermic-isobaric conditions. A set of solid solutions of the $\mathrm{S1}_x\mathrm{S2}_{1-x}\cdot q\mathrm{W}$ composition is crystallized in this system. It does not matter, whether the solid solutions form the continuous set or whether they have a miscibility gap. The combination of phase and chemical equilibrium conditions and Gibbs-Duhgem equation gives us the following equation connecting mole fraction ($x$) of the first component ($\mathrm{S1}\cdot q\mathrm{W}$) in solid phase ($s$) with component activities ($a$) in liquid phase ($l$):

$$x^{(s)}_{\mathrm{S1}\cdot q\mathrm{W}} = \frac{d\ln a^{(l)}_{\mathrm{S1}} + q\, d\ln a^{(l)}_{\mathrm{W}}}{d\ln a^{(l)}_{\mathrm{S2}} - d\ln a^{(l)}_{\mathrm{S1}}}$$

(Differentials correspond to infinitesimal motion along solubility curve). In the case of solid solutions without water the above-mention equation becomes simpler:

$$x^{(s)}_{\mathrm{S1}} = \left(1 - \frac{d\ln a^{(l)}_{\mathrm{S1}}}{d\ln a^{(l)}_{\mathrm{S2}}}\right)^{-1}$$

Thus, if one has the analytical dependence (model of electrolyte solution) of activity components for liquid phase and the data of saturated solution compositions, we can theoretically reconstruct entire phase diagram. And vice versa, we can confirm the consistency of experimental data for liquid and solid phase compositions.

The KCl – KBr – $H_2O$ system at 25°C is presented as an illustration.

## POSTER: B 4

# MOLECULAR MODELS OF AGGREGATION PHENOMENA IN LIQUID MIXTURES: THERMODYNAMIC AND RELATED PROPERTIES

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The modeling of the aggregation phenomena in molecular mixtures with emphasis to study both supramolecular organization and molecular nature of a set of physicochemical (thermodynamic, dielectric, optic, and kinetic) properties are reviewed.

The hierarchy of the models of supramolecular species mixtures based on the consecutive description universal dispersion, dipolar, repulsive and specific such as H-bonds intermolecular interactions has been considered. Models of polyvariable supramolecular species as regard to structure and composition of different topology (chain-like, cyclic, comb-like, etc.) as well as the methods for describing the structure, electric (dipole moment) and optical (polarizability tensor) properties of those are discussed. The Quasichemical Model of Nonideal Solution (QCNAS) which describes thermodynamic properties of the strongly non-ideal aggregated mixtures was developed [1,2]. The aggregation processes are described in terms of the activities of species and thus equilibrium constants are transferable.

The description of thermodynamic functions of mixing (Gibbs energy, enthalpy, entropy) of non-electrolytes mixtures with complex character of the supramolecular ordering in the whole composition range and wide temperature range is considered. The influence of the supramolecular ordering on the excess functions of mixtures and phase equilibria is discussed.

The formulas for dielectric (permittivity) and optical (refractive index and its scalar and tensor fluctuation derivatives, defining Rayleigh light scattering phenomena) properties of molecular liquids with thermodynamic and structural parameters of the aggregation were established.

The mobile supramolecular aggregates in molecular liquids (alcohols, amides, amines, etc., and their mixtures with solvents of different nature (inert, solvating, associating, etc.)) were revealed. The thermodynamic parameters of the supramolecular ordering were defined.
The macroscopic manifestations of the supramolecular organization of liquid systems in physicochemical properties are discussed.

This work was supported by the State Support Program of Leading Research Schools (Contract ? 02.445.11.7071) and the Russian Foundation for Basic Research (Project N 04-03-32819).

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# POSTER: B 5

## NOVEL RELATIONSHIPS BETWEEN THE GC RETENTION TIMES OF PCB ISOMERS UNDER ISOTHERMAL CONDITIONS AND THEIR MOLECULAR TOPOLOGICAL DESCRIPTORS

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It has been many reports on the relationship between capillary gas chromatograph retention times (GC-RTs) and the molecular descriptors calculated on the basis of the molecular structure such as solvent accessible surface area or the molecular topological indexes. Using various chemoinformatic techniques, the relationship has been revealed in order to predict the various physicochemical properties, for example, solubility, *n*-octanol/water partition coefficients, and Henry's low constants. However, a detail analysis on the times for tested molecules is difficult, because the RTs are observed under the programmed temperature conditions, and they depend on the change in the capillary temperature [1]. Therefore, a precise prediction for the physicochemical properties becomes to be also difficult by using supervised learning in terms of the RTs.

In the present study, the GC-RTs of PCB, which have been known as very serious environmental contaminants, were observed under isothermal conditions, and marked difference of GC-RTs was found under two conditions, the programmed and the isothermal temperature, as shown in Figure 1.

We have already pointed out that there is a novel relationship between topological indexes, $\chi^2$ and $\chi^3$, and the GC-RTs, and that the number of chlorine atoms substituted at proximitive position (Npx-Cl) plays an important role in elucidation of the relationship between GC-RTs and physicochemical properties for PCB 209 congeners [2]. By using the RTs obtained in the present study, we predicted and re-evaluated the more acute aqueous solubility of PCB isomers such as trichloro biphenyls in terms of the molecular topological indices including Npx-Cl as the descriptors.

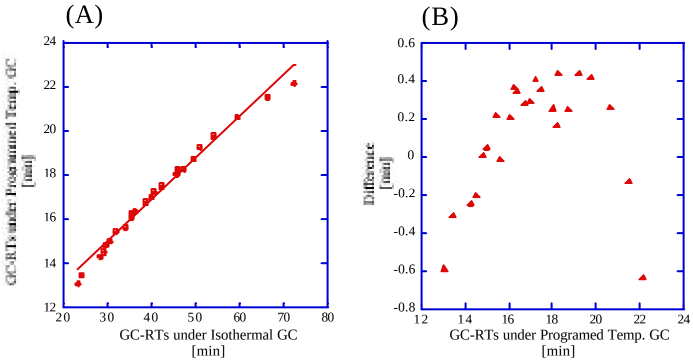

Fig. 1; (A) The relationship of RTs obtained from two programmed temperature conditions.
A line in the figure shows the simple regression equation.
(B) The differences calculated from the regression equation.

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## POSTER: B 6

# EXTENDED GROUP CONTRIBUTION METHOD FOR STANDARD THERMODYNAMIC PROPERTIES OF AQUEOUS KETONES, ETHERS, AND ESTERS

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We have compiled and/or recomputed literature data on thermodynamic properties at the standard state of infinite dilution (partial molar volume and heat capacity, hydration enthalpy and Gibbs energy) in aqueous solutions of some oxygen-type organic compounds – ketones, ethers and esters in a wide range of conditions ($T < 673$ K, $p < 40$ MPa). Various related quantities such as Henry's law constants, infinite dilution activity coefficients, solubilities were also included in compilation and converted to standard thermodynamic properties.

Functional groups contained in these solutes were treated by the group contribution method in combination with the Sedlbauer-O´Connel-Wood equation of state (SOCW EOS, ref. [1]). For the values of hydration enthalpy and hydration Gibbs energy at reference conditions, which are needed in the SOCW model as integration constants, we applied a consistent group contribution approach of Plyasunov et al. (ref. [2] and references therein). Parameters of the SOCW EOS for carbonyl, ester and ether structural elements were determined by simultaneous weighted correlation of collected experimental data. Second-order corrections are incorporated to improve description of data. The model was verified by comparison of computed and experimental results.

This method extends the group contribution scheme for standard thermodynamic properties of aqueous hydrocarbons presented recently [5]: in correlations we retained the already determined parameters of hydrocarbon segments and evaluated the SOCW parameters only for the carbonyl, ether and ester groups. The extended method can be used for prediction of standard partial molar volumes and heat capacities, hydration enthalpies and Gibbs energies, chemical potentials, Henry's law constants, air-water distribution coefficients etc. of aliphatic alkanes, alkenes, cycloalkanes and benzene and their derivatives with -OH, -O-, -CO-, -COO- functional groups at temperatures to 600 K and pressures to 50 MPa.

Collected data are a part of project Database of recommended values on hydration properties, carried out under auspices of the International Union of Pure and Applied Chemistry and the International Association for the Properties of Water and Steam.

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# POSTER: B 7

## SOLUBILITIES OF ALKYNE COMPOUNDS

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It is likely that ethyne was first made in the laboratory by Edmund Davy in 1836 and rediscovered by Bertholet about a quarter of a century later. The latter gave it the name *acetylene*. Since then it has become a cheap rare material for organic synthesis and for use as fuel. It has a high enthalpy of formation and heat of combustion. It forms an explosive mixture with air over a wide range of composition. The pure gas can explosively decompose to its elements at pressures above 206 Pa but is stable to higher pressure when in solution. The gas is very sparingly soluble in water. Much experimental work has been carried out to find good organic solvents for absorption of the gas. Compounds containing oxygen or nitrogen tend to be good solvents. The ways in which different types of organic solvents behave are shown graphically. Detailed evaluations of these data have been published (1).

The higher gaseous alkynes also have high positive enthalpies of formation but are stable in the gas phase. Propyne, 1-butyne, 2-butyne, 1,3-butadiyne (*diacetylene*) and 1-buten-3-yne (*vinylacetylene*) are gases at $25^{?}$C and atmospheric pressure. Higher 1-linear alkynes are liquid to C16 and, in general, have lower melting points than 2-alkynes of the same chain length. 1-Buten-3-yne is an important industrial chemical. At present other higher gaseous alkynes have limited applications but removal from gas streams is often important.

The available experimental measurements of solubility in water and in organic solvents are limited to propyne, 1-butyne, 1,buten-3-yne and 1,3-butadiyne. Good organic solvents contain oxygen or nitrogen. The available data has been evaluated where possible. Diagrams show the general pattern of behaviour in comparison with that of ethyne.

The solubilities of organic gases in water may be predicted from their chemical structure using the EPI Suite$^{TM}$ which may be downloaded for private use from the Internet (2). Solubilities of higher alkynes can thus be estimated and compared with experimental data for the lower alkynes.

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# POSTER: B 8

## ESTIMATION OF ENVIRONMENTAL COMPARTMENT HALF-LIVE CLASSES FROM STRUCTURAL SIMILARITY

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Environmental fate models require the input of compartment specific half-lives. There is almost no general estimation method for compartment half-lives available, and the few existing models address only some individual degradation processes with particular importance. Here, a k nearest neighbours approach is applied to obtain semi-quantitative predictions from a reference set of environmental half-live data from literature for ca. 300 compounds. For a given chemical, the most similar compounds from the reference set are selected by means of an atom-centred fragment approach, and the half-live class is predicted from the reference values of the selected neighbours. The results of this method are compared to methods for degradation rates of individual processes, and the reliability is tested by statistical means.

## POSTER: B 9

# PROPERTY PREDICTION MODEL SELECTION BASED ON STRUCTURAL SIMILARITY

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To select among several prediction methods the presumably best-performing scheme for a given property and compound, a method based on prediction errors evaluated for structurally similar compounds is presented. The similar compounds are selected through analysis of atom-centred fragments (ACFs) in accord with a k nearest neighbour procedure in the 2-dimensional structural space. As an example, the technique is applied to water solubility prediction. Seven estimation methods for the water solubility of organic compounds are selected, and a reference set of 1876 compounds with validated experimental values is used to analyse the performance of the approach. The discussion includes possible improvements of the selection procedure, and alternative approaches to improve the performance of prediction methods.

# POSTER: B 10

# PREDICTION OF THE AIR/WATER PARTITION COEFFICIENT – FRAGMENT MODELS VS. LFER

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The partition coefficient air/water (Henry's law constant in water) is one of the most important properties in environmental fate modelling. There is a number of fragment models available to predict the partition coefficient directly from the 2D molecular structure. An alternative approach is the LSER equation applying Abraham parameters. The latter has a solid mechanistic background, but a drawback in practice is the limited availability of the Abraham parameters for substances of interest. Typically, more complex compounds require the estimation of Abraham parameters from chemical structure. The reliability of air/water partitioning predictions by fragment models and LSER models with experimental and predicted descriptors is analysed and compared for a large reference set of validated experimental partition coefficients. In this context, particular emphasis is devoted to a proper characterisation of the applicability domains of the different prediction methods.

# POSTER: B 11

## CHEMICAL DOMAIN OF PROPERTY PREDICTION MODELS

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To develop a property prediction model, a training set is required. The application domain of such a model is restricted by the model space covered by the training set. The chemical domain is a particular aspect of the model application domain. The latter cannot generally be characterized in terms of compound classes, because there are many multifunctional compounds that cannot be allocated to a particular compound class. The approach suggested here employs atom-centred fragments (ACFs) to characterize substructures and their chemical contexts occurring in the training set. The chemical domain is described in terms of the type and frequencies of ACFs. The usefulness of this approach and the effect of chemical domain violations are demonstrated with examples of models for physical-chemical properties of environmental relevance.

# POSTER: B 12

## THERMODYNAMIC PROPERTIES OF SUPERCRITICAL FLUIDS: EXAMPLE OF ARGON

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Accurate information on the thermodynamic properties of supercritical fluids is highly sought for the chemical technology, especially, supercritical extraction technology. The thermodynamic properties of fluids near the critical region are strongly affected by the presence of fluctuations and therefore, can not be described by conventional equation. We have investigated the behavior of the thermodynamic properties of argon in the vicinity of the critical region. For this reason we have used the so-called the crossover model to describe the thermodynamic properties of argon in a wide range of temperatures and densities around the critical point.

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# POSTER: C 1

## ENVIRONMENTAL AND EFFECTIVE SOLAR SEA-SALT PRODUCTION

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Thermodynamic simulations of the systems $Na^+$, $K^+$, $Mg^{2+}$ /$SO_4^{2-}$, $Cl^-$//$H_2O$; $Na^+$, $K^+$, $Ca^{2+}$ /$SO_4^{2-}$, $Cl^-$//$H_2O$; $Na^+$, $Ca^{2+}$, $Mg^{2+}$ /$SO_4^{2-}$, $Cl^-$//$H_2O$ and $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ /$SO_4^{2-}$, $Cl^-$ //$H_2O$ in the temperature range –5 to 40°C was done. The thermodynamic Pitzer model was used. The results were applied to sea water solar evaporation after treatment with different Ca and Mg solutions. Prognoses concerning the crystallization sequence and the pure NaCl yield were made. Laboratory and large-scale experiments were organized on the basis of theoretical data. A scheme was proposed for enlargement of the NaCl crystallization field and increasing the NaCl yield by 20% in the sea water system. A method for raw salt purification and table salt preparation was also suggested.

The system $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$/$Cl^-$, $CO_3^{2-}$//$H_2O$ was thermodynamically simulated at 5 – 40°C. The results were applied to waste brines remaining after sea-salt production and a method for large $MgCO_3.3H_2O$ crystals preparation was proposed. The optimal conditions of the processes were determined. Laboratory and large-scale experiments were carried out. The product obtained was with a food grade quality.

The implementation of both schemes for NaCl and $MgCO_3.3H_2O$ production in the solar sea-salt industry will be positive with respect to economy and for ecology.

**Acknowledgements**: This work was done with the financial support of the EC FP6, PROJECT INCO –CT-2005-016414

# POSTER: C 2

## EFFECT OF PLASTICIZERS ON THE RHEOLOGICAL PROPERTIES OF HIGH MOLECULAR WEIGHT ATACTIC POLY(VINYL ALCOHOL) SOLUTIONS

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Poly(vinyl alcohol) (PVA) is a semicrystalline polymer having hydroxyl groups that give rise to inter- and intramolecular hydrogen bondings. The molecular weight is a fundamental factor affecting physical properties of PVA. Generally, viscosity of aqueous PVA solutions is considered to be a function of molecular weight and concentration of PVA. Rheology is important in the formulation of polymeric materials, preparing them for the fabrication process. As a result, for materials such as fibers, films, and gels, it is a prerequisite to investigate the rheological properties of such materials. Most plasticizers used in PVA applications enhanced the flexibility as an interfere to the inter and intramolecular hydrogen bonds of PVA. We investigated rheological behaviours of solutions of high molecular weight atactic PVA with different ratios in glycerin/polyethylene glycol (PEG) (v/v) mixture. It is noted that in this study, at lower frequency, *G'* of glycerin/PEG (0/10, v/v) solution was much lower than those of homo PVA solution and glycerin/PEG (10/0, v/v) solution.

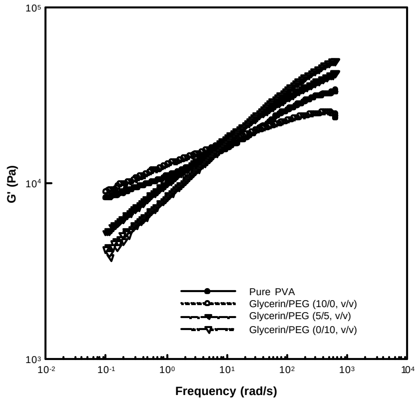

Fig. 1: Storage moduli of high molecular weight a-PVA solutions with plasticizers in different ratios of glycerin/PEG (v/v) mixture.

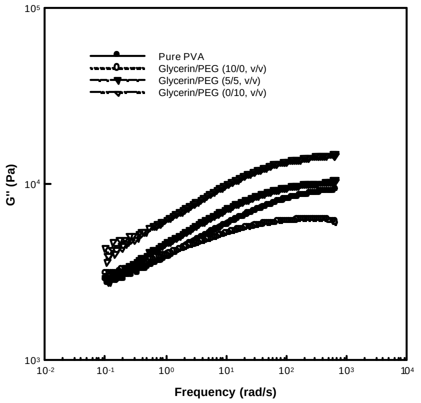

Fig. 2: Loss moduli of high molecular weight a-PVA solutions with plasticizers in different ratios of glycerin/PEG (v/v) mixture.

**Acknowledgements**

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# POSTER: C 3

## RHEOLOGICAL CHARACTERIZATION OF CONCENTRATED SOLUTIONS OF RECYCLED POLY(VINYL ALCOHOL)

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Poly(vinyl alcohol) (PVA) gels are easily formed via physical pathway. Most PVA solutions, including PVA/water solution, are well known to form thermally reversible gels. The high-performance PVA fiber can be obtained by using gel spinning. The performance of the fiber is obviously affected by the forming conditions of gel. Therefore, it is essential to control process parameters in order to obtain the desired structure of the gel materials. The processing parameters could be considered as gel concentration, temperature, pressure, and filler content. The viscoelastic behaviour of recycled PVA solutions was investigated in oscillation mode. The recycled PVA solutions of concentrations 19%, 21%, and 23% were, respectively tested at 70? . Figs. 1 and 2 shows the change of the dynamic storage modulus G' and loss modulus G" of recycled PVA/dimethyl sulfoxide (DMSO) solutions with various concentration. As the recycled PVA concentration was increased, viscosity also was increased. However, 21% and 23% solutions showed similar results in slopes.

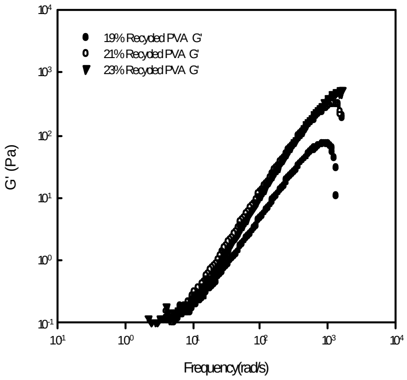

Fig. 1: G' of recycled PVA/DMSO solutions at three different concentrations with frequency.

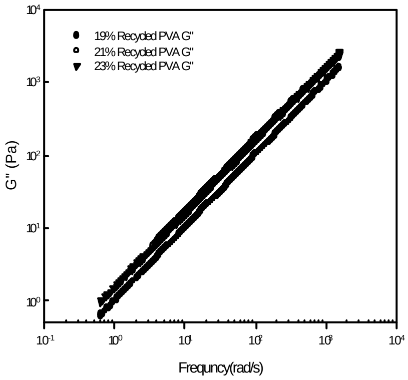

Fig. 2: G" of recycled PVA/DMSO solutions at three different concentrations with frequency

## Acknowledgements

This almost work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE).

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# POSTER: C 5

## INFLUENCE OF SOME PARAMETRERS OF POLY(VINYL ALCOHOL) [PVA] HYDROGELS SYNTHESIS ON THEIR SWELLING CHARACTERISTICS AND STABILITY

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The aim of this paper is to present the influence of some parameters of PVA hydrogels synthesis, such as number of repeated freezing and thawing cycles, initial PVA solution concentration and freezing temperature on the hydrogels microstructure and consequently on their swelling behaviour.

PVA hydrogels obtained by freezing and thawing technique are heterogeneous, porous, white, opaque, elastic gels, showing a high mechanical resistance.

All the parameters of hydrogels synthesis that affect the ice crystals formation will affect the porosity of hydrogels.

Some thermodynamic and kinetic considerations on the hydrogel swelling process have been made.

The stability of the obtained PVA hydrogels has been discussed in terms of PVA molecules leaching from the gel network during the swelling process. The hydrogel stability has been correlated with the above mentioned synthesis parameters.

The hydrogels swelling capacity, their stability and porosity are very important properties for biomedical application and for their use in separation processes (membranes permittivity and sorption processes).

Taking into account the exceptional properties of PVA, such as water solubility, biodegradability, biocompatibility, non-toxicity, non-carcinogenity, capacity of gel formation via chemical or physical routs, these types of environmental friendly hydrogels could be tailored for various applications.

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# POSTER: C 6

## MODELLING OF A THERMO-HYDRO-CHEMICAL COUPLED PROBLEM USING GEOSYS/ROCKFLOW

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The object-oriented FEM simulator GeoSys/RockFlow is a comprehensive software for the modelling of highly coupled thermo-hydro-mechnical-chemical (THMC) processes. It is applied to non-isothermal multiphase multicomponent reactive transport in deformable porous media as well as deep HLW (high-level waste) repositories for prediction of long-term performance [1]. Concerning the, the geochemical simulator PHREEQC is coupled into the program for reactive transport simulation ([2], [3]). This paper provided simulation results of a hypothetical repository with engineered barrier system (highly compacted bentonite) located in crystalline rock for saturated and unsaturated cases under assumption of equilibrium geochemical reactions under the framework of the international DECOVALEX IV THMC project. With heat generation, the temperature in the near field arises to as much as 93°C. Drying process occurs at the early 20-40 years of operation and can result in swelling/shrinking effect in bentonite that influences the effective porosity alteration. In order to reveal the temperature dependence of the geochemical reactions, the database of PHREEQC has been modified according to EQ3/6 and GEMS geochemical databases. The chemical effect on the long-term swelling/shrinking of bentonite is simulated by a newly developed chemical swelling model, which is based on the diffuse double layer (DDL) theory and connects the microstructural mineral properties with the macroscopical swelling effect. To simulate the flow process, the modified Richard’s model is adopted that taking account of the vapour transport into consideration. These models or functions have been verified by experiments or by comparison with the results by other source codes.

2D simulation results showed that temperature affects not only multiphase flow but also geochemical reactions. At the early stages, it was observed that the sample dried at the heated end due to evaporation. Consequently, capillary pressure was increased at the heated end and this enhanced the flow rate. An effect on chemical reactions was also observed in the simulation. Changing the temperature caused variation of ionic concentrations in bentonite porewater. Dissolution/precipitation of solid minerals is also closely related to the temperature change. The long-term effect shows that dissolution/ precipitation of minerals in bentonite are controlled by the steady state downward flow, which keeps the replacement of porewater in bentonite with the inflow of porewater in granite. Therefore, geochemical reactions between bentonite porewater with the minerals in bentonite cannot reach equilibrium state.

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# POSTER: C 7

## INORGANIC CHEMICAL SPECIES IN THE WATER SYSTEM RIVER-ESTUARY-SEA. SOME CASE STUDIES

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Water basins are influenced by different natural and anthropogenic factors which change their mineral composition. The chemical species present in them depend on the medium properties such as composition, ionic strenght, salinity, acidity and redox potential. They undergo numerous changes downstream from river to the sea, especially in estuary and sea zones, where the mixing of different water types occurs.

The case studies were two different polluted Bulgarian rivers, Kamchiya and Ropotamo, during the years 2004-2006. The total concentrations of major elements (Na, K, Mg, Ca, C, S), of the trace elements (Fe, Mn, Cu, Zn, Cd and Pb), of nutrients (N, P) and of the dissolved oxygen were determined experimentally. The results were used for thermodynamic modeling of the inorganic chemical species in the systems. Ion-association model, computer program PHREEQCI version 2.11, and a new database sst2005.dat were used for this purpose. A great variety of complexes in the studied system were established due to the anion concentrations and the coordination ability of $Me^{n+}$ ions.

The predominant chemical species in all *river – estuary – sea* system are as follows:

- major elements Na, K, Mg, Ca, Cl, trace elements Mn, Zn and Cd are present mainly as free ions;
- Fe as hydroxy form: $Fe(OH)_2^+$;
- Cu and Pb as free $Me^{+2}$ and $MeCO_3^0$ ions ;
- S as $SO_4^{2-}$ ions;
- C as $HCO_3^-$ ions;
- N is as free $NO_3^-$ and $NO_2^-$ ions.

Inorganic P is found in different species in the system. In river waters the predominating species are $H_2PO_4^-$ and $HPO_4^{2-}$, while in sea waters the concentration of $H_2PO_4^-$ decreases by 1-2 orders of magnitude.

The species $Fe(OH)_3^0$ and $Fe(OH)_4^-$ quickly increase with the solution acidity.

In sea water, the species $MSO_4^0$ (M = Mg, Ca), $MgHCO_3^+$, $NaSO_4^-$ and $NaHCO_3^0$ exist due to the high concentration of the $SO_4^{-2}$ and $Cl^-$ ions, and high acidity. The concentration of $Me(SO_4)_n^{2-2n}$ and $MeCl_n^{2-n}$ (Me=Mn, Zn, Cd; n=1÷4) increase rapidly and $CdCl_n^{2-n}$ (n=1-3) prevails.

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