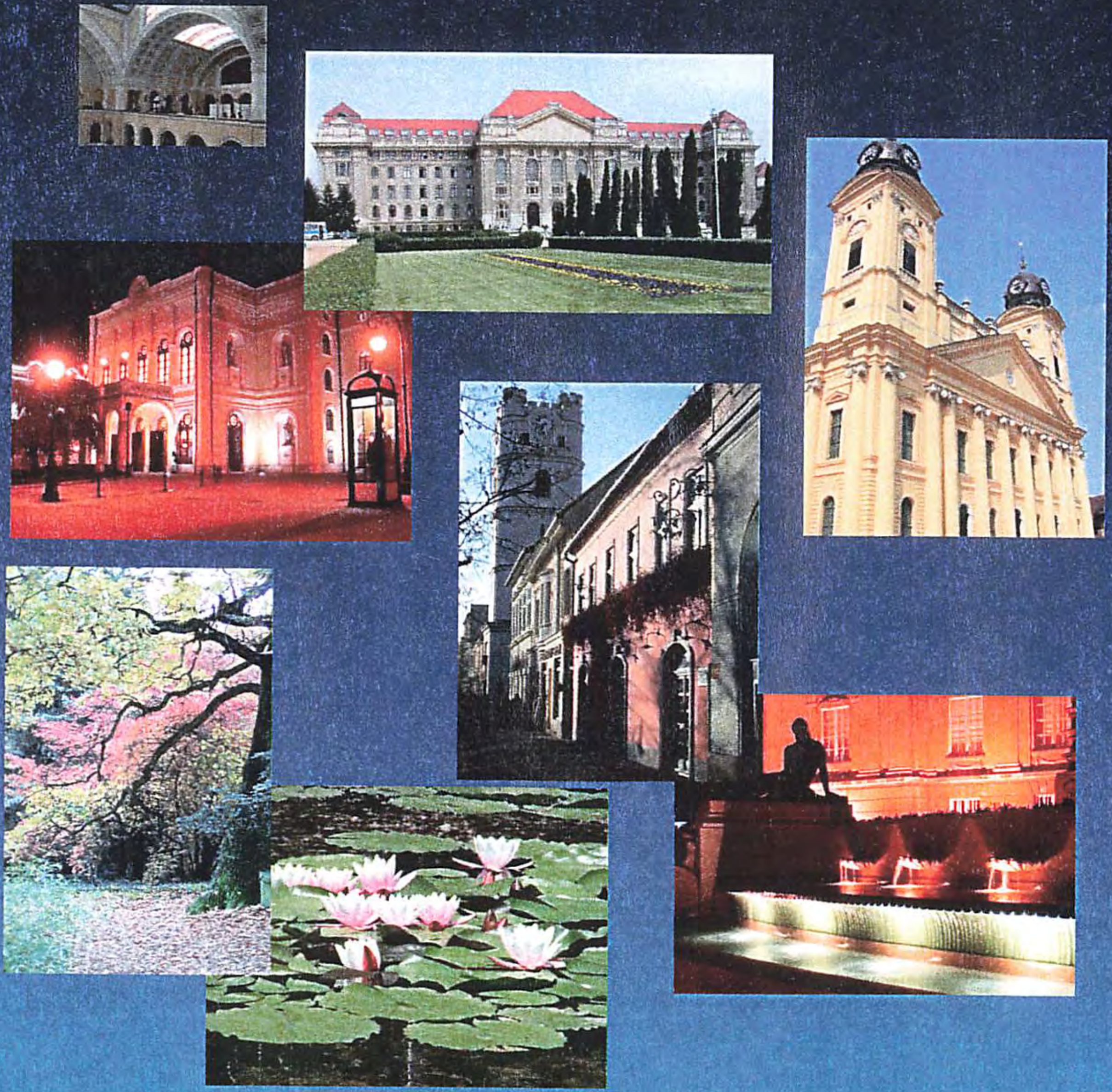
Toshio Yamaguchi

28th International Conference on Solution Chemistry

August 23-28, 2003
Debrecen, Hungary



Book of Abstracts

Welcome to the 28th International Conference on Solution Chemistry

August 23-28, 2003
Debrecen, Hungary

Book of Abstracts

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István Lázár

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(in alphabetical order)

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Saturday, August 23

	Central Building
20^{00}	**Welcome Reception**

Sunday, August 24

	Ceremony Hall	
9^{00}	**Opening**	
9^{30}	József Szejtli: Properties of cyclodextrins and their inclusion complexes in aqueous solutions **A-PL2** *(Chairperson: Ingmar Persson)*	
10^{20}	Benjamin Schwartz: Optical control of the electron in the simplest charge transfer reaction **A-PL1** *(Chairperson: Ernő Keszei)*	
11^{10}	Coffee break	
	Lecture Hall IX	Lecture Hall XI
11^{40}	Rudi van Eldik: Electronic tuning of the lability of inert metal complexes **A-I1** *(Chairperson: György Bazsa)*	Achim Mueller: Nano Water Drops in Highly Charged Porous Nanocontainers Reveal "Water" Structure-Problems – with and without Solutes **D-I1 MSPOM** *(Chairperson: Josef Barthel)*
12^{10}	Tünde Megyes: Structure determination of some ruthenium and iron complexes by X-ray diffraction **A1**	Marc Henry: New perspectives concerning water structure **D1 MSPOM**
12^{40}	Lunch	

(Table continued)

(Sunday, August 24)

14^{30}	Mikhail Maliarik: Metastable Complexes with Pt-Tl Bonds in Solution: Structure, Equilibria, and Dynamics **A-I2** *(Chairperson: Magnus Sandström)*	Tianbo Liu: Supramolecular Structures Formed by Soluble Giant POM ions in Dilute Solution: A New Solute State for Inorganic Ions **D-I2 MSPOM** *(Chairperson: Dirk Kurth)*
15^{00}	Péter Nagy: Formation kinetics of direct Pt–Tl bonded cyano-complexes **A3**	Michael Pope: Manipulating Polyoxometalates? **D2 MSPOM**
15^{20}	Shin-Ichi Ishiguro: Conformational Change of Solvent N,N-Dimethylpropionamide upon Coordination to the Manganese(II) Ion **A2**	Lage Pettersson: Quantitative NMR Spectroscopy - An excellent tool **D3 MSPOM**
15^{40}	Dmitry Kagan: Analysis of the thermodynamic and structure data internal consistency for binary liquid alkali-metal mutual solutions ~~**A4**~~ D9	Masato Hashimoto: Recent Progress of Peroxopolyoxometallates **D4 MSPOM**
16^{00}	Coffee break	
16^{20}	Zareen Abbas: Old and New about the Hydroxide Ion in Aqueous Solution **A5** *(Chairperson: László Simándi)*	Francis Taulelle: Rational Design of Crystal Tectonics Driven by in-situ NMR **D5 MSPOM** *(Chairperson: Julius Glaser)*
16^{40}	Alexander Apelblat: Volumetric and thermal properties of some electrolyte solutions **A6**	Christian Burger: Aggregation behavior of fullerene surfactants in aqueous solution **D6 MSPOM**
17^{00}	János Mink: Infrared Raman and Theoretical Studies of Metal-Oxygen Bonding of Complexes Existing in Solutions **A19**	Franziska Groehn: Model Polyelectrolytes: Electrostatic Self-Assembly and Nanotemplating **D7 MSPOM**
17^{20}	Rakesh Bhardwaj: Excess molar volumes and viscosotiesfor binary mixtures of alkoxyethanols with substituted and cyclic amides at 298.15 K **A8**	
19^{00}	Dinner	

Monday, August 25

	Ceremony Hall		
9^{00}	Peter Stang: Nanoscale Molecular Architecture: Design and Self-Assembly of Metallacyclic Polygons and Polyhedra via Coordination **D-PL1** *(Chairperson: Anna Proust)*		
9^{50}	Dirk Kurth: Organization of metallo-supramolecular modules in tailored architectures **B-PL1** *(Chairperson: Vojko Vlachy)*		
10^{40}	Coffee break		
	Lecture Hall IX	Lecture Hall XI	Lecture Hall XII
11^{10}	Antal Rockenbauer: Free radical encapsulation in cyclodextrin: Enhanced stability of spin trapped superoxide radicals **B-I1** *(Chairperson: Staffan Sjöberg)*	Stefanie Kramer: Interactions of low molecular drug compounds with lipid bilayers **C-I1** *(Chairperson: Lage Pettersson)*	Hitoshi Ohtaki: The Structure of Hydrogen-Bonding Liquids at High Temperaturtes and High Pressures **E-I1** *(Chairperson: Tamás Radnai)*
11^{40}	Ian Snook: A Microscopic Simulation of the Viscous Flow of Colloids **B1**	Ivan Kron: Interactions of uric acid - consequences for uric acid urolithiasis **C1**	Ariel Chialvo: Hydration and Na+Cl- Pair Association in High-Temperature Aqueous Solutions along Sub- and Supercritical Isotherms **E1**
12^{00}	Andrea Bencini: Phosphate ester hydrolysis promoted by novel di- and trinuclear Zn(II) complexes with macrocyclic ligands **B2**	Alexei K. Baev: Novel Approaches to the Structure of Functional Solvents and Elementarorganic Compounds with Saturated Hydrocarbon Ligands **C2**	Zadja Atik: Volumetric Studies of Binary and Ternary Aqueous Solutions Containing 2,2,2-Trifluoroethanol, Alcohols and Acetone at Temperature 298.15 K and Pressure 101 kPa. **E2**
12^{20}	Sándor Kéki: Monitoring the reactions of polymers by MALDI-TOF Mass Spectrometry **B3**	Tamás Gajda: Solution chemistry of dialkyltin(IV) - peptide interaction: equilibrium and structure **C3**	Toshio Yamaguchi: Structure of supercritical alcohol-water mixtures **E3**
12^{40}	Lunch		
14^{30}	**Poster session**		
19^{00}	Dinner		
20^{00}	**Concert**		

Tuesday, August 26

	Ceremony Hall		
9^{00}	Peter Cummings: Computer simulation of solutions-simple and complex **F-PL1** *(Chairperson: Achim Müller)*		
9^{50}	Walter Leitner: Supercritical Carbon Dioxide as a "Green Solvent" for Catalysis **E-PL1** *(Chairperson: Ferenc Joó)*		
10^{40}	Coffee break		
	Lecture Hall IX	Lecture Hall XI	Lecture Hall XII
11^{10}	Yizhak Marcus: Standard Partial Molar Volumes of Ions in Solvents **A-I3**) *(Chairperson: Glenn Hefter*	Henryk Kozlowski: Solution Studies on Cu(II)-Peptide Systems Related to Neurodegenerative Diseases **C-I2** *(Chairperson: Kiyoshi Sawada)*	Tamás Radnai: Structure of high concentrated solutions **E-I2** *(Chairperson: Toshio Yamaguchi)*
11^{40}	Emanuel Manzurola: Volumetric and thermal properties of some electrolyte solutions **A9..**	Attila Jancsó: Hydrolytic cleavage of ribonucleotide monophosphates and heterodinuclear metal complexes of a polyalcohol ligand **C4**	Mitsuhiro Kanakubo: Development of High-Pressure Magnetic Resonance Imaging for In-Situ observation of Supercritical Fluid Solutions **E4**
12^{00}	Gábor Lente: Photooxidation of water by 2,6-dichloro-1,4-benzoquinone **A10**	M. Amelia Santos: Bis(3-hydroxy-4-pyridinone) derivatives of aminoacids and their metal-complex formation equilibria **C5**	Hitoshi Kanno: Variation of hydrogen bond strength with solute concentration in glassy aqueous electrolyte solutions **E5**
12^{20}	Andrej Horvat: The influence of CO_2 on the solubility of amorphous sodium disilicate **A11**	Masaaki Tabata: Enhanced conformational changes of DNA in the presence of Mercury(II), Cadmium(II) and Lead(II) porphyrins in aqueous solution **C6**	Josef Sedlbauer: Thermodynamic properties of dilute NaCl(aq) solutions near the critical point of water **E6**
12^{40}	Lunch		
14^{00}	**Excursion to Hortobágy**		

Wednesday, August 27

	Ceremony Hall		
9^{00}	Helmut Sigel: Acid-Base Properties of Purines and the Effect of Metal Ions **C-PL1** *(Chairperson: Imre Sóvágó)*		
9^{50}	Vincenzo Balzani: Molecular devices and machines **D-PL2** *(Chairperson: Attila Horváth)*		
10^{40}	Coffee break		
	Lecture Hall IX	Lecture Hall XI	Lecture Hall XII
11^{10}	Ronald Fawcett: Studies of Anion Solvation in Polar Aprotic Solvents **A-I4** *(Chairperson: Willis Forsling)*	Michael Probst: Molecular dynamics of iron cations in water **F-I1** *(Chairperson: Manfred Zeidler)*	Magnus Sandström: Sulfite solution species by sulfur spectroscopy **G-I1** *(Chairperson: Hisanobu Wakita)*
11^{40}	Haruhiko Yokoyama: Regular structure change of liquids on liquid-liquid mixing due to existence of micriscopic molecular groups **A12**	Nataliya Atamas: Theoretical Studies of Ethanol-Water Soluitions at Various Concentrations **F1**	Kiyoshi Sawada: Complex formation of biodegradative chelate agents **G1**
12^{00}	Paula Gameiro: Aqueous solution studies on copper(II)fluoroquinolone complexes **A13**	Pierre Turq: Molecular Hydrodynamics: from Kubo to Smoluchowski **F2**	Vladimir Simeon: Existence of two UV spectrometrically distinguishable forms of nitrate ion in dilute aqueous solutions **G2**
12^{20}	Levente Nádasdi: Catalytic hydrogenation with rhodium-phosphatriazaadamantane-complexes **A14**	Gergely Tóth: Iterative determination of pair potentials from diffraction data **F3**	Andrey Vishnikin: Indirect spectrophotometric and atomic-absorption determination of some elements by means of polyoxometalates **G3**
12^{40}	Lunch		

(Table continued)

14^{30}	Josef Barthel: Electrolyte conductivity from infinite dilution to saturation in protic, aprotic and low dc solvents **A-I5** *(Chairperson: Gábor Jancsó)*	Vojko Vlachy: Electrolyte adsorption in disordered porous material **F-I2** *(Chairperson: Richard Buchner)*	Michel Meyer: Solution studies of mono- and ditopic macropolycyclic receptors incorporating 5,12-dioxocyclam units **C-I3** *(Chairperson: Henryk Kozlowsky)*
15^{00}	Marija Bester R.: Ion pair formation of 2,2-electrolytes in water from electric conductivity measurements **A15**	Hartmut Krienke: Theoretical calculations of ion hydration with different water models **F4**	Krystyna Krot-Lacina: The first reported Ru(III)-hydroxamate complexes speciation studies, structures and comparison with Fe(III)- hydroxamates **C7**
15^{20}	László Almásy: Small-angle neutron scattering study of aqueous solutions of 1,2 hexanediol **A16**	Andrei Lyashchenko: Structural dynamics of water and its spectra of orientational polarization **F5**	Valerio Di Marco: Electrospray Ionization Mass Spectrometry in Studies on Aluminium(III)-Ligand Solution Equilibria **C8**
15^{40}	Simon Erenburg: Structure of new heterometallic Ru/Cu,Ni complexes in water solution and hexane by XAFS spectroscopy **A17**	Isao Okada: MD simulation of crystal growth of NaCl from its supersaturated aqueous solution **F6**	Nick Hadjiliadis: Interactions of Histone H_2A Peptides with Cu(II) and Ni(II). Hydrolysis and Oxidative Properties of the Species Formed **C9**
16^{00}	Coffee break		
16^{20}	Mats Lindberg: NMR study on some metal O,O'-dialkyldithiophosphates **A18** *(Chairperson: Tianbo Liu)*	László Pusztai: Reverse Monte Carlo modelling of the microscopic structure of aqueous electrolyte solutions **F7** *(Chairperson: Walter Leitner)*	Maria Rangel: Solution Studies of 3-Hydroxy-4-Pyridinones with Biomedical Applications **C10** *(Chairperson: Michael Meyer)*
16^{40}	Ufuk S. Vural: The Charge-Transfer Complexes of The Macromolecular Calixarene Compound with Electron Acceptors **A7**	Humberto Saint-Martin: A comparative molecular dynamics study of the hydration of lanthanide (III) cations using ab initio based polarizable model potentials **F8**	András Gorzsás: Simple blood tests of potentially insulin mimetic peroxovanadates **C11**
17^{00}	Hisanobu Wakita: Structural Analysis of Al-EDTA Complexes in Aqueous Solution by means of NMR and X-ray absorption spectra **A20**	András Baranyai: The fluctuation theorem for ideal mixtures **F9**	Béla Gyurcsik: Solution equlibria of a de novo designed multidentate ligand with transition metal ions **C12**
17^{20}	Roman Nashiour: Dielectric relaxation spectroscopy of aqueous hexyltrimethylammonium bromide solutions **A21**	Azzedine Abbaci: Thermodynamic properties of ethane in the critical region **F10**	Zoltán Szakács: Acid-base chemistry of folic acid, methotrexate and related bioligands **C13**
17^{40}	Mobolarinwa Bilewu: Cleaning of Photoresist and Etch Residue from Low-k Dielectrics using Supercritical CO_2 **A25**		
19^{00}	**Banquet**		

Thursday, August 28

	Ceremony Hall		
8^{30}	Christian Reichardt: Solvatochromic Dyes as Empirical Indicators of Solvent Polarity-Some New Findings **G-PL1** *(Chairperson: Tamás Kiss)*		
9^{20}	Coffee break		
	Lecture Hall IX	Lecture Hall XI	Lecture Hall XII
9^{50}	Ingmar Persson: The Influence of Short Strong Hydrogen Bonding in Alkyl-N-iminodiacetic acid on Structure, Properties and Complex Formation Ability **A-I6** *(Chairperson: Shin-Ichi Ishiguro)*	Anna Proust: Activation of functionalised polyoxometalates : stories in solution **D-I3** *(Chairperson: Peter Stang)*	Richard Buchner: Micelle hydration and dynamics in aqueous SDS solutions **G-I2** *(Chairperson: Marc Henry)*
10^{20}	Glenn Hefter: Thermodynamics of Transfer of Ions from Water to Aqueous Organic Mixtures **A22**	Vladimir Durov: Supramolecular assemblies in liquids: structure, thermodynamics, and macroscopic properties **D8**	Anatolii Zakharov: Some questions about effect of composition of a solution on properties of cellulose **G4**
10^{40}	Yasuhiro Umebayashi: Raman Spectroscopic study on the Solvent conformation change upon Solvation to metal ion **A23**	Sarah Tolbert: New Electronic Materials through Cooperative Self-Organization of Zintl Clusters and Surfactants ~~**D9**~~ A4	Mihály Braun: Leaching of Glaze Elements of Historic Ceramics to Liquid Medium **G5**
11^{00}	Takuhiro Otsuka: Specific Cation Effect on Quenching Reactions by Negatively Charged Complexes in Aqueous Solutions **A24**	Andrea Bodor: The mechanism of the Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene **D10**	
	Ceremony Hall		
11^{25}	**Closing**		
12^{00}	Lunch		

Plenary lectures

A-PL1

Optical Control of the Electron in the Simplest Charge Transfer Reaction

Benjamin J. Schwartz

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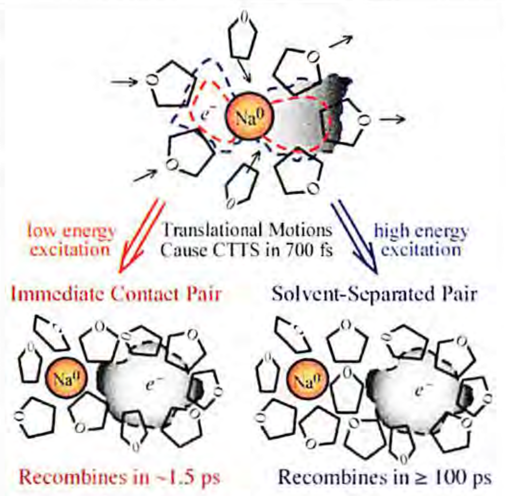

Figure 1: Schematic representation of the molecular motions involved in the ejecting of an electron from Na^-. At low excitation energies, the excited state wavefunction spans only the region inside the first solvent shell (red contour). Higher excitation energies produce excited-state wavefunctions with more curvature, which can extend past the first solvent shell (blue contour). For either type of excitation, translational solvent motions cause detachment of the excited electron after 700 fs. For low energy excitation, the electron is ejected nearby the Na parent, resulting in an immediate contact pair that undergoes recombination in 1.5 ps (lower left). Higher energy excitation produces some probability that the electron localizes one solvent shell away from the parent, leading to a stable solvent-separated contact pair that does not recombine for hundreds of ps.

This talk focuses on the use of femtosecond spectroscopic techniques to unravel the motions of the solvent molecules responsible electron transfer (ET) from single atoms to nearby cavities in the solvent. Single-atom systems allow direct spectroscopic access to the effects of solvent motions on the reactant's electronic structure without interference from vibrations or rotations. We have fully characterized the spectroscopy of our system of choice, the sodium anion, which now represents the only electron transfer reaction for which the spectrum of the reactant, its excited state, and both products are fully known and can be monitored independently as the reaction progresses. We find that ET is rate-limited by the translational solvent motions that accommodate the change in size of the reactants as the electron detaches. Moreover, by comparing the behavior of the solvated electrons produced via charge transfer to those created by direct ionization, we have inferred many of the molecular details of electron transfer reactions, including: the distance electrons are ejected following excitation, the stability of the resulting atom:electron contact pairs, and the fact that back ET from solvent-separated atom:electron pairs occurs slowly because it is in the Marcus inverted regime. Our picture as to how the electron transfer proceeds in this model system is summarized in Figure 1.

Our detailed characterization of the ET process in the Na^- system also has allowed us to use a sequence of femtosecond laser pulses to control the reaction. We can select the distance at which the electron localizes from its Na atom partner (either in an immediate or solvent-separated contact pair) by proper choice of the excitation wavelength used to eject the electron. Once ejected, the electrons in these contact pairs undergo a spontaneous back ET reaction to regenerate the parent Na^-. By exciting the electron near 2000 nm immediately after it is ejected, we can alter the course of the ET reaction. We find that when the 2000-nm pulse is applied to electrons in immediate contact pairs, the back ET process is shut off. This is because the delocalization of the electron's wavefunction that occurs upon 2000-nm excitation increases the probability to find the electron outside the immediate solvent cavity, where it can no longer undergo rapid back electron transfer. In a similar experiment in which the 2000-nm pulse is applied some time after the electron is ejected, all the electrons in immediate contact pairs have recombined into sodium anions, so the only electrons left to absorb the 2000-nm light are in solvent-separated contact pairs. Delocalizing the electronic wavefunction in the solvent-separated pair gives some probability to increase the electron density in the adjacent cavity that contains the sodium atom, enhancing the rate of the back ET. There is also some probability that the excited electrons can localize even further from the Na atom, so that the 2000-nm pulse both enhances and hinders the back electron transfer reaction. With a careful analysis of the data, we have been able to unravel exactly how far the electron moves when excited at 2000 nm, allowing us to manipulate the electron-sodium atom distance at any time during the back electron transfer reaction that we choose. This represents a degree of optical control over electron transfer reaction dynamics that has yet to be achieved for the nuclear degrees of freedom in photodissociation reactions. [See *Science* **293**, 462-5 (2001); *JACS* **124**, 7622 (2002)]

A-PL2

Properties of Cyclodextrins and their inclusion complexes in aqueous solutions

Prof. József Szejtli

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In the family of cyclic oligosacharides the α-, β-, and γ-cyclodextrins (consisting of 6, 7, and 8 glucopyranose units linked by α-1,4 glucosidic linkages) and their chemically modified derivatives deserve particular attention, on account of their specific, and widely utilized useful properties. The cyclodextrins and most of their numerous derivatives are soluble in water, creating apolar regions in the hydrophilic aqueous system.

The CDs are generally conical toroid-like structures, their outer surface is hydrophilic, surrounded by a hydrate-shell, while their internal axial cavity, and the narrower entrance of the cavity (primary hydroxyl side) is of hydrophobic character. Therefore, adding to aqueous CD solutions any more or less hydrophobic, poorly soluble substance, whose molecules (or a part of the molecules, e.g. a side-chain) are geometrically compatible with the CD cavity, inclusion complex will be formed: the apolar molecule or its appropriate moiety) will be included into the CD cavity (= "host" molecule). The primary result is, that the solubility of the so-called guest molecule increases, its reactivity frequently modified: increases or decreases depending on the depth of the penetration of the guest into the host. Spectral properties will be significantly modified: by NMR spectroscopy the structure of the formed complex can be determined exactly. Fluorescence or luminescence intensity, circular dichroism, frequently even the UV spectra are modified. Diffusion, membrane permeation rates are strongly modified upon CD complexation.

Examples will be presented for the effects attainable by CD-inclusion complexation and their industrial application in pharmaceutical industry, biotechnology, chromatographic separations, remediation of polluted environment, etc.

B-PL1

Modulat Materials Synthesis: From structure to function

Dirk G. Kurth

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Versatile methodologies are presented to combine, position, and orient functional metallo-supramolecular modules in well-defined hierarchical architectures based on metallosupramolecular polyelectrolytes and polyoxometalate clusters as functional and amphiphiles as structural components, respectively. Multi-component sequential self-assembly is employed in systematic ways to assemble the materials. The modularity of this approach provides extensive control of structure and function from molecular to macroscopic length scales. Structure-property relationships of these functional supramolecular materials are discussed. Results from self-assembled nanostructures, thin films, liquid crystalline phases, as well as mesophase will be presented. In particular, electro- and photochromic as well as catalytic properties are implemented into the final device architecture. In addition, methods are developed to assemble, manipulate, and characterize well-defined nanostructures at surface.

Recent Publications:

D. G. Kurth, P. Lehmann, M. Schütte *Proc. Natl. Acad. Sci. U. S. A. 97* (**2000**) 5704.
D. G. Kurth, N. Severin. J. P. Rabe *Angew. Chem. 114* (**2002**) 3833.
D. G. Kurth, A. Meister, A. Thünemann, G. Förster *Langmuir* **19** (2003) 4055-4057.
S. Liu, D. G. Kurth, B. Bredenkötter, D. Volkmer *J. Am. Chem. Soc.* **124** (2002) 12279-12287. D. Volkmer, B. Bredenkötter, J. Tellenbröker, P. Kögerler, D. G. Kurth, P. Lehmann, H. Schnablegger, D. Schwahn, M. Piepenbrink, B. Krebs *J. Am. Chem. Soc.*, **124** (2002) 10489-10496.

C-PL1

Acid-Base Properties of Purines and the Effect of Metal Ions

Helmut Sigel

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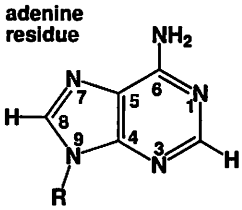
The predominant tautomeric structures of the common purine nucleobases and their proton binding sites have been established about five decades ago[1] and (macro) acidity constants for the release of protons in aqueous solution are known.[1-3] However, the insight that the intrinsic proton affinities, as quantified by so-called micro acidity constants, are needed to understand the chemistry of nucleobases, e.g., their metal ion-binding properties, is of much newer date.[1]

Since the basicities of the ring nitrogens of N9-substituted purines decrease in the order N1 > N7 > N3,[4] the acidity, e.g., of $(N7)H^+$ in an adenine residue can only be measured under conditions where N1 also carries a proton and of course, the positive charge at $(N1)H^+$ facilitates the deprotonation of $(N7)H^+$. Clearly, for sophisticated comparisons one would like to know the (micro) acidity constant of $(N7)H^+$ under conditions where N1 is free. Such micro acidity constants can only be derived by indirect procedures, e.g., by methylation of certain sites;[4] they allow the conclusion, e.g., for $H(adenosine)^+$ $pk^{N7\text{-}N1}_{H\cdot N7\text{-}N1}$ being 2.2, that the ratio [N7-N1·H]/[H·N7-N1] equals 25:1 in aq. solution.



Among other systems, the acidifying properties of N7-coordinated divalent metal ions on the corresponding (N1)H sites in several guanine derivatives have been studied. The acidification of N7-bound M^{2+} on (N1)H decreases in the following series: Cu^{2+} (Δ p$K_a = 2.2 \pm 0.3$) > Ni^{2+} (1.7 ± 0.15) > Pt^{2+} (1.4 ± 0.1) ≈ Pd^{2+} (1.4). Furthermore, it can be shown[5] that, e.g., the acidifying effect of Pt(II) at N1 on $(N7)H^+$ is reciprocal and equals the effect of N7-coordinated Pt(II) on (N1)H.

Supported by the Swiss Nat. Sci. Found. and the Swiss Fed. Off. for Educ. & Science (COST D20).

(1) Martin, R. B., *Acc. Chem. Res.* **1985**, *18*, 32-38; *Met. Ions Biol. Syst.* **1996**, *32*, 61-89.
(2) Sigel, H.; Lippert, B., *Pure Appl. Chem.* **1998**, *70*, 845-854.
(3) Sigel, H.; Song, B., *Met. Ions Biol. Syst.* **1996**, *32*, 135-205.
(4) Kampf, G.; Kapinos, L. E.; Griesser, R.; Lippert, B.; Sigel, H., *J. Chem. Soc., Perkin Trans. 2* **2002**,1320-1327.
(5) Griesser, R.; Kampf, G.; Kapinos, L. E.; Komeda, S.; Lippert, B.; Reedijk, J.; Sigel, H., *Inorg. Chem.* **2003**, *42*, 32-41.

D-PL1

Nanoscale Molecular Architecture: Design and Self-Assembly of Metallocyclic Polygons and Polyhedra via Coordination

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The use of just two types of building blocks, linear and angular, in conjunction with symmetry considerations allows the rational design of a wide range of metallocyclic polygons and polyhedra. via the coordination motif.[1-3] We have used this approach to self-assemble a variety of molecular polygons such as triangles, rectangles, squares etc. More recently we have used this methodology to construct via self-assembly the following polyhedra: truncated tetrahedra, cubooctahedra[4] and dodecahedra[5], as well as other high symmetry cages. The methodology is illustrated in Figure 1. These novel, supramolecular ensembles are characterized by physical and spectral means. The design strategy, formation, characterization and potential uses of these novel metallocyclic assemblies will be discussed, along with our recent results in crystal engineering.

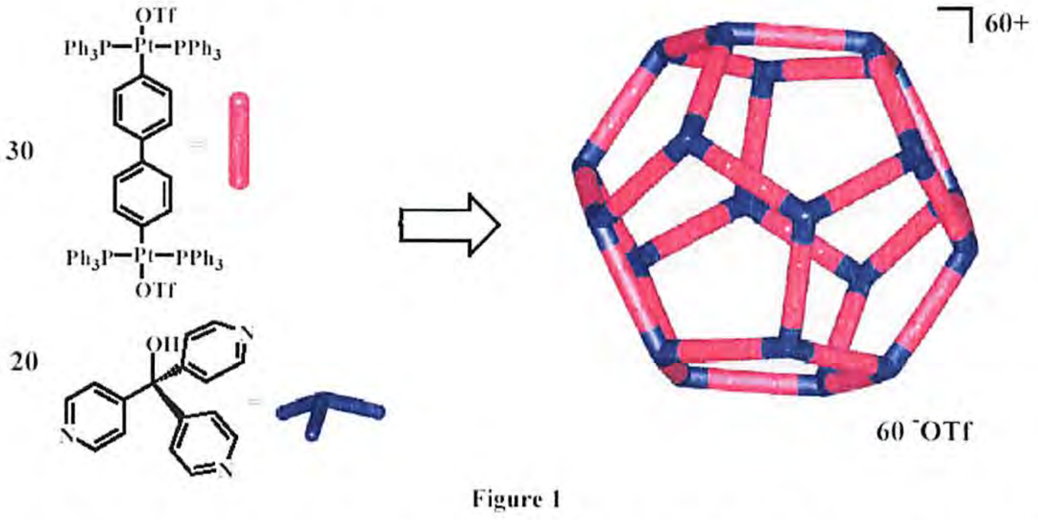

Figure 1

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D-PL2

Molecular devices and machines

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The macroscopic concepts of a device and a machine can be straightforwardly extended to the molecular level [1-4]. A *molecular–level* device can be defined as an assembly of a discrete number of molecular components (that is, a *supramolecular* structure) designed to achieve a specific function. Each molecular component performs a single act, while the entire assembly performs a more complex function, which results from the cooperation of the various molecular components. A *molecular–level machine* is a particular type of molecular–level device in which the component parts can display changes in their relative positions as a result of some external stimulus. This definition points out that spontaneous movements caused by thermal energy, including a recent demonstration of the rotation of a single molecule on a surface, have nothing to do with the concept of molecular-level machine. It should also be noticed that, although there are many chemical compounds whose structure and/or shape can be modified by an external stimulus (see, e. g., the photoinduced *cis–trans* isomerization processes), the term molecular–level machines is only used for systems showing large amplitude movements of molecular components.

Molecular–level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, are characterized by *(i)* the kind of energy input supplied to make them work, *(ii)* the way in which their operation can be monitored, *(iii)* the possibility to repeat the operation at will (cyclic process), *(iv)* the time scale needed to complete a cycle, and *(v)* the performed function.

In this lecture, we will illustrate examples of: (a) molecular-level devices for the transfer of electrons or electronic energy; (b) molecular–level devices capable of performing extensive nuclear motions (i.e., molecular machines); (c) molecular level systems whose functions imply the occurrence of both electronic and nuclear rearrangements.

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E-PL1

Supercritical Carbon Dioxide as a “Green Solvent” for Catalysis

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Carbon dioxide in its supercritical state ($scCO_2$) has received considerable attention recently as a new reaction medium for chemical synthesis [1] and in particular for catalysis [2]. Its lack of toxicity and ecological hazards as well as its high miscibility with reaction gases make $scCO_2$ a very attractive solvent. The possibility to tune its solubility properties by variation of pressure and temperature opens a wide range of fascinating applications, including innovative approaches to catalyst recycling and immobilization.

In the present contribution, we will discuss current developments in the application of $scCO_2$ as reaction medium for synthesis and catalysis from our laboratories. It will be shown that $scCO_2$ can not only replace common organic solvents in a wide range of processes but allows at the same time to broaden the scope of many synthetic methodologies. Recent progress toward a rational utilization of the physical and chemical properties of $scCO_2$ for the control of catalytic reactions will be a major theme. In particular, new approaches for the immobilisation of organometallic and enzymatic catalysts based on the rich phase behaviour of supercritical reaction media will be presented.

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F-PL1

Molecular Simulation and Modeling of Water and Aqueous Solutions in Bulk and at Interfaces

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Abstract

For two decades, our group has been involved in (largely theoretical) research on water and auqueous solutions. In this talk, we will review our simulation and theoretical research on water and aqueous solutions, both in bulk and at interfaces (particularly metal oxide interfaces). Topics include the development of intermolecular potentials for water, ion pairing in supercritical water, the electrical double layer at the 110 surface of rutile, and water nanoconfined between mica surfaces.

G-PL1

Solvatochromic Dyes as Empirical Indicators of Solvent Polarity Some New Findings

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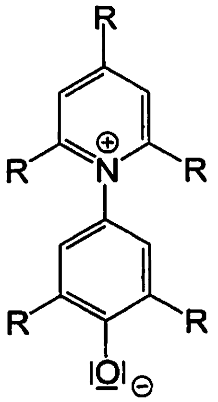
The extraordinarily large negative solvatochromism of4-(2,4,6-triphenylpyridmium-l-yl)-2,6-diphenylphenolate, **la**, has been used to establish UV/Vis spectroscopically an empirical scale of solvent polarity, called $E_T(30)$ resp. E_T^N scale.[1] $E_T(30)$ values are available for a great variety of pure solvents, binary and ternary solvent mixtures, microheterogeneous and polymer solutions, as well as for various kinds of surfaces.[1,2] Without changing the basic zwitterionic chromophore with its long-wavelength solvent-dependent intramolecuar charge-transfer absorption, the five peripheral phenyl groups of the standard betaine dye **la** can be replaced by other groups *(i.e.* substituted phenyl, 2-, 3-, and 4-pyridyl, etc.) in order to adapt this highly solvatochromic indicator dye to a great variety of further useful applications, all using its high sensitivity to small changes in its surroundings.[3–5]



In this report, syntheses, solvatochromic properties, and some practical applications of these pyridinium *N*-phenolate betaine dyes in various fields of interest, particularly in solution and analytical chemistry,[1,6] will be reviewed. Their thermochromism, piezochromism, halochromism, and chiro-solvatochromism will be also shortly mentioned.

R = phenyl, substituted phenyl,
pyridyl, and others; all five R = phenyl ⟶ **la**

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Invited lectures

A-I1

Electronic tuning of the lability of inert metal complexes

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The lability of inert metal complexes of Co(III) and Pt(II) can be systematically tuned through the variation of σ-donor and π-acceptor effects introduced by the spectator ligands. In the case of Co(III) complexes the substitution behaviour is largely affected by the presence of a single metal-carbon bond as found in co-enzyme B_{12}. In recent years, we have undertaken systematic mechanistic studies of the effect of a single metal-carbon bond on the substitution behaviour and lability of vitamin B_{12}, modified vitamin B_{12}, as well as model Co(III) complexes, in order to unravel the fascinating influence of such a metal-carbon bond.[1-4]

The associative substitution behaviour of inert Pt(II) complexes can also be tuned by a combination of σ-donor and π-acceptor effects.[5,6] We have undertaken detailed studies where these effects are varied in a systematic way, by first considering the influence of π-acceptor effects and then the combination of σ-donor and π-acceptor effects.[5,6] A detailed account and overall mechanistic picture for these substitution processes will be presented.

The ability to tune the lability, and therefore the reactivity, of inert metal complexes is of potential significance for the application of such complexes in biological and catalytic processes. A general outlook will be presented.

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A-I2

Metastable Complexes with Pt-Tl Bond in Solution: Structure, Equilibria, and Dynamics

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A new family of heteronuclear cyano compounds incorporating transition (Pt) and main group (Tl) metals bound with a non-buttressed Pt-Tl bond was synthesised in aqueous solution. The metal-metal linkage is formed in the reaction between platinum and thallium in their stable oxidation forms, Pt(II) and Tl(III), or *vice versa*: Pt(IV) and Tl(I). Four binuclear complexes with a general composition $[(CN)_5Pt\text{-}Tl(CN)_n(aq)]^{n-}$ (n = 0-3) and a trinuclear species $[(NC)_5Pt\text{-}Tl\text{-}Pt(CN)_5]^{3-}$ were identified and structurally characterised in solution by multinuclear NMR, EXAFS and vibrational spectroscopy.[1,2] The complexes exist in equilibrium in solution.[3]

The compounds are capable to undergo a photoinduced electron transfer between the coupled hetero-metal ions. Upon irradiation into the metal-to-metal charge transfer (MMCT) absorption band, effective photoredox reaction takes place. It results in scission of the Pt-Tl bond and formation of various complexes of oxidised platinum (Pt(III, IV)) and reduced thallium (Tl(I)).

The heteronuclear Pt-Tl cyano compounds can be further modified in terms of their stability, solubility, and light absorption characteristics. It has been found that the platinum pentacyano unit of the species is inert towards the tested ligands, whereas the thallium "part" of the complexes can be tuned significantly. Apart from water, dimethylsulphoxide has been found to be a suitable solvent for the Pt-Tl bonded cyanide compounds. Solvatochromism of the MMCT and electron transfer in the complexes have been also studied.

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A-I3

Standard Partial Molar Volumes of Ions in Solvents

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The standard partial molar volumes of many electrolytes, mainly uni-univalent, in various solvents are known [1]. These can be separated into the ionic values by accepted assumptions. These values consist of the sum of the intrinsic volume, the (negative) electrostriction, and any solvent structural effects. Intrinsic volumes of ions were recently published [2]. The electrostriction for an ion (i) in a solvent (s) can be calculated from the pressure dependence of the relative permittivity, according to the Benson & Copeland [3] expression:

$$V_{\mathrm{el}}(\mathrm{i,s}) = (N_{\mathrm{Av}}z(\mathrm{i})^2e^2/8\pi\varepsilon_0)\varepsilon(\mathrm{s})^{-1}r(\mathrm{i})^{-1}[\partial\ln\varepsilon(\mathrm{s})/\partial P]_T$$

The more elaborate shell-by-shell calculation according to Marcus and Hefter [4] may provide more accurate values, using consecutive *j* values:

$$V_{\mathrm{el}}(\mathrm{i,s,M\&H}) = -(8\pi^2N_{\mathrm{Av}}\varepsilon_0)\Sigma[r(j)^3 - r(j-1)^3]\{\varepsilon(j)[(\partial\ln\varepsilon/\partial P)_T - \kappa_{\mathrm{T}}] + \kappa_{\mathrm{T}}\}E(j)^2$$

For hydrogen bonding solvents: water, MeOH, EtOH, EG, FA, NMF, and NMA, and for dipolar aprotic solvents, such as acetone, PC, $MeNO_2$, MeCN, DMF, and DMSO, the calculated values agree well with the experimental ones without requiring a structural term. The shell-by-shell calculation appears to be the more accurate one for cations but the simpler one is better for the anions if the electrostriction is appreciable. For very large (hydrophobic) ions a structural term is required, fitted with group contributions, but cannot as yet be independently estimated.

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A-I4

Studies of Anion Solvation in Polar Aprotic Solvents

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Electrolyte solvation in polar aprotic solvents is to a large extent determined by solvation of the anion. The majority of electrolytes which are soluble in these liquids involve polyatomic anions with a mononegative

charge, such as perchlorate and tetrafluoroborate. However, electrolytes with monoatamic anions such as the larger halides (bromide and iodide) are also soluble in solvents with higher permittivities. In this connection we have studied the effects of LiBr and LiI on the FTIR spectra of acetonitrile (AcN) and dimethylsulfoxide (DMSO). Earlier work[1] showed that the perchlorate anion has a small effect on the -C≡N stretching frequency in AcN.

In this paper the effects of the anions on the band associated with the polar group in AcN and DMSO is described and discussed. The effects of the anions on the CH_3 groups is also described. *Ab initio* quantum chemical calculations carried out as part of this study are presented. These results help with the interpretation of the infrared data and give a detailed picture of anion solvation in these solvents.

* Presenting author

A-I5

Electrolyte conductivity from infinite dilution to saturation in protic, aprotic and low dc solvents.

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Representative electrotyte solutions of all solvent classes are studied from infinite dilution to saturation by the use of low concentration chemical models and AMSA. The co-operation of the models reproduces satisfactorily for technical use the experimental conductivity curves over the whole concentration range and at various temperatures. Limiting conductivities, association constants, distance parameters and the maxima of specific conductivities are basic information for pure and applied solution chemistry.

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(to be continued).

A-I6

The Influence of Short Strong Hydrogen Bonding in Alkyl-*N*-iminodiacetic Acids on Structure, Physico-Chemical Properties and Complex Formation Ability

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Alkyl-*N*-iminodiacetic acids with varying alkyl chain length have been prepared and characterized with respect to structure, acidic properties and ability to form aggregates in water.[1] The solid alkyl-*N*-iminodiacetic acids have a unique structure with neutral zwitterionic units linked together into polymer chains through short strong hydrogen bonds, *d*(O(-H)···O) ≈ 2.46 Ĺ, and where the ν(O-H) stretching vibration at ca. 720 cm^{-1} supports the presence of such a hydrogen bond.[1] The polymer chains are cross-linked together to bilayers through relatively strong hydrogen bonds between ammonium and carboxylate groups, and where the parallel alkyl groups are interdigitating each other; the bilayer surface consists of hydrophilic iminodiacetic acid groups. The difference in acidic and complex formation properties of alkyl-*N*-iminodiacetic acids, present as monomers, and large aggregates, as e.g. n-octadecyl-*N*-iminodiacetic acid, in water[1,2] will be presented and discussed.

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B-I1

Free radical encapsulation in cyclodextrin: Enhanced stability of spin trapped superoxide radicals

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The spin trapping technique is a powerful tool to detect free radicals in biological milieu. The superoxide radical is a key species in oxidative stress and its trapping can be solved by the application of various nitrons. Adequately long stability could be achieved by DEPMPO (5-diethoxyphosphoryl-5-methyl-1-pyrroline-N-oxide), but in the presence of reducing agents like ascorbate, α-tocopherol or glutathion the nitroxide spin adducts are reduced to the ESR-silent hydroxylamines. To protect the nitroxide radicals we applied biocompatible molecules, like cyclodextrines, which can form inclusion complexes with the trapped radicals.

By using various nitrons (DEPMPO, DMPO, EMPO) and different cyclodextrines (e.g. methyl-β-cyclodextrin) an order of magnitude increase was found in the lifetime of trapped radicals[1]. While the protection against the gluthathione peroxidase initiated transformation was almost perfect, the efficiency was only partial against ascorbic acid, but even in this case the DEPMPO and EMPO adduct of superoxide radicals can be observed for a few minutes.

Acknowledgements: This work was supported by the Hungarian National Research fund, OTKA T-032929.

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C-I1

INTERACTIONS OF LOW MOLECULAR DRUG COMPOUNDS WITH LIPID BILAYERS

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Mammalian cells are multi-compartment systems. The separating membranes consist of a vast variety of lipids and proteins in characteristic patterns according to their function. The interaction of drug compounds with different membrane domains is relevant for their behavior in the body. To get insight in drug-membrane interactions, unilamellar liposomes (artificial lipid bilayer vesicles) were used *in vitro* to study the pH-dependent affinity of acidic and basic drugs to lipid bilayers by means of equilibrium dialysis. The partitioning profiles in a phosphatidylcholine liposome/buffer system followed Henderson-Hasselbalch functions with higher affinities of the neutral than the ionized drugs. With liposomes containing negatively charged lipids such as oleic acid above pH 6 or phosphatidylinositol, the affinity of the protonated base propranolol to the membrane increased but not the one of the neutral molecule. These findings contribute to the predictability of interactions between lipophilic drugs and membrane domains.

To measure membrane permeation of solutes, we developed an assay to follow the entry of aromatic carbonic acids into the lumen of Tb^{3+}-containing liposomes. Upon entry the aromatic carbonic acids increase the luminescence of Tb^{3+}. With this assay we could demonstrate that the cell penetrating peptide TAT(44-57) is not able to cross lipid bilayers in a liposomal system.

Combining the two assays we can directly compare affinity and permeation of solutes to and across lipid bilayers with defined lipid compositions simulating particular cell membrane domains.

C-I2

Solution Studies On Cu(II)-Peptide Systems Related To The Neurodegenerative Diseases

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The role of redox metals like copper, iron or manganese in neurodegenerative disorders was not a major subject of interest among a neuroscience community before ninties.[1] One of the most exciting development has been reached recently in the studies on the elucidation of the role of SOD1 in the familial amyotropic lateral sclerosis (FALS).[2] Copper may be also a critical factor in the development of Alzheimer disease (AD).[1,3] The βA4 amyloid precursor protein (APP) is able to bind and reduce very effectively Cu(II) ions, which may change drastically the fate of APP and its fragments.[4] Metal ions may also induce the amyloid formation at nanomolar concentrations. Creutzfeldt-Jacob disease (CJD) and related TSEs, similarly to AD, are characterized by neuroamyloid formation.[5] There is increasing evidence that normal isoform of PrP binds copper and the complex formed posses a strong anti-oxidant activity, which could be a vital factor for synaptic homeostasis.[6] The studies on the Cu^{2+} binding abilities by cysteine-rich fragment of APP strongly suggest that three histidyl residues may play a critical role in the interactions between metal ion and protein in the developments of the disease.[7,8] The potentiometric, NMR, EPR, CD and related spectroscopic studies on the Cu^{2+} binding to protein fragments may help to elucidate the metal ion involvement in the neurodegeneration mechanisms as it will be discussed in the lecture.[9]

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C-I3

Solution studies of mono- and ditopic macropolycyclic receptors incorporating 5,12-dioxocyclam units

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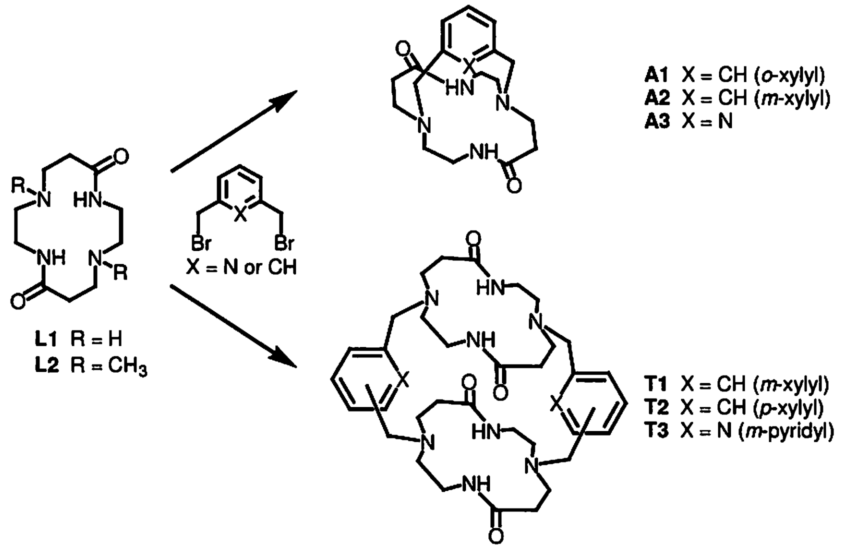
The quest for new macropolycyclic receptors that could serve as functional catalysts or as biomimetic models of biological systems, is stimulating continuous endeavor aimed to design new synthetic strategies. A *trans* "autodiprotected" cyclopeptide having 5,12-disposed carbonyl groups, was found to provide a convenient entry into a new and highly preorganized class of ligands possessing well defined but tunable metal-binding cavities.[1] Provided that 5,12-dioxocyclam (**L1**) was reacted with the appropriate biselectrophile, macrobicyclic and macrotricyclic cages of spheroïdal (**A1-A3**) and cylindrical (**T1-T3**) topologies were obtained, respectively.



The peculiar protonation properties of these ligands will be discussed in light of crystallographic, potentiometric and calorimetric results.[2] Intramolecular hydrogen bonding accounts for both the slow protonation kinetics of **A3** and the strong allosteric effect displayed by **T1**. The latter phenomenon is reminiscent to the activity regulation mechanism of some enzymes.

Abstraction of the amide protons by a weak base afforded stable and inert nickel(II) and copper(II) complexes. Selective metalation of **T1** enabled to isolate both the mono- and the dicopper species. Selected structural and spectroscopic properties, including metal-metal interactions in the dinuclear species, will be also presented.

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D-I1 MSPOM

Nano Water Drops in Highly Charged Porous Nanocontainers Reveal "Water" Structure-Problems – with and without Solutes

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Metal-oxide-based capsules containing up to 100 water molecules and different electrolytes are described. The surfaces of the capsules are covered with nanoscale pores, which – when open – permit entry of water and solutes into the cavities, while variations of the capsule properties – such as charge and the nature of the internal surface – greatly influence the encapsulated species. This allows to get more detailed information about the water structure and the influence of electrolytes on it.

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D-I2 MSPOM

Supramolecular Structures Formed by Soluble Giant Polyoxomolybdate Ions in Dilute Solution: A New Solute State for Inorganic Ions

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Abstract: It is widely accepted that soluble inorganic ions tend to distribute homogeneously in solution. But this universal solute state is found to be not valid anymore for the giant ions of polyoxomolybdates (POM) and their derivatives. These nanoscale anions, regardless their shapes, masses, number of charges, exist as single ions when they are just dissolved in a polar solvent (e.g., water, ethanol or acetone). However, this is not their most stable state. They tend to continuously and very slowly further associate into uniform, spherical vesicle supramolecular structures containing over 1000 individual POM anions, as determined by laser light scattering techniques. The vesicle structures represent a second solute state for inorganic ions, possibly preferred by giant anions containing multiple charges. The vesicle structures are different from the vesicles formed by surfactants in that there is no hydrophobic part in POM anions. Unique water nano-assemblies are believed to exist between adjacent POMs in the vesicles, providing additional driving force to minimize the repulsive forces for the vesicle formation, along with the balance between van der Waals force and electrostatic interactions. The discovery of the POM supramolecular structure finally answers the long-time puzzle of "molybdenum blue solutions" -- the aggregation behavior of various highly soluble, unique nanosized and structurally well-defined POM molecules in polar solvents. The POM anion assembly represents a model system to link the solution behavior of simple inorganic ions and that of polyelectrolytes, and will help to develop a deeper understanding of the formation of colloids with hydrophilic surfaces. Many exciting new physical phenomena can be expected in future investigations.

D-I3

Activation of Functionalized Polyoxometalates : Stories in Solution

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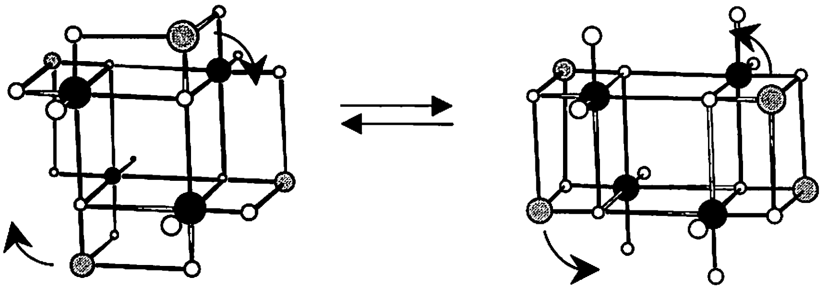
Polyoxometalates are soluble oxides of groups 5 and 6 metals. They can be functionalized through the formal replacement of some {M=O} functions by others : we have thus described nitrogeneous derivatives including nitrosyl, organo-diazenido, organo-imido and nitrido ligands.[1] Functionalization is attractive, since it can provide stabilization of otherwise unstable species, new precursors for catalytic precursors, new building blocks for material chemistry through remote functionality, activation of the surface oxygen atoms... On the basis of multinuclear NMR and electrochemical data, we will show how the electronic properties of the polyoxometalate are tuned.

In its broadest acceptation, functionalization of polyoxometalates also include the grafting of an organometallic moiety at their surface. More generally, we have been interested in organometallic oxides. We will focus on the $[M_4O_{16}\{Ru(arene)\}_4]$ species, which present a fluxional behavior in some cases, as it has been evidenced in solution by multinuclear NMR and EXAFS. Both the windmill and the triple-cubane isomers have been characterized.



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E-I1

THE STRUCTURE OF HYDROGEN-BONDING LIQUIDS AT HIGH TEMPERATURES AND HIGH PRESSURES

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Structures of some hydrogen-bonding liquids have been investigated by means of solution X-ray diffraction, NMR and Raman spectroscopy.

Water keeps the hydrogen-bonding structure at high temperatures and high pressures up to the density of ca. 0.7 g cm^{-3}, and the water-water interatomic distance was practically unchanged at 293 pm over the wide density range of 0.7 – 0.95 g cm^{-3}. On the other hand, the coordination number of water molecules monotonously decreased from about 4.4 at ambient temperature and pressure to 1.5 – 1.7 at high temperatures and pressures. From these experimental results it is concluded that the homogeneous-looking water phase was microscopically heterogeneous and it consists of small clusters, in which water molecules interact each other through hydrogen bonds, and gas-like, practically monomerly dispersed water molecules.1)

Formamide is another typical hydrogen-bonding liquid, which forms head-and-tail type linear chains and ring dimers in the network. With the increase in the temperature, the hydrogen-bonding structure was decomposed and ring dimer moieties changed to linear type structure. On the other hand, more compact ring dimer moieties than linear type structure were enhanced to be formed in the network with elevating pressure.1)

N-Methylformamide (NMF) has been concluded to form linear type chain structure.2) The effect of temperature and pressure on the liquid structure of NMF is being investigated by Raman spectroscopy and the solution X-ray diffraction method.

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E-I2

Structure of high concentrated solutions

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The usual structural studies, performed by either diffraction experiments or theoretical calculations, are mainly restricted to relatively low or medium concentrated solutions: up to several mol dm^{-3} of solute concentration. These studies are aiming at hydration/solvation structures, structure of bulk solvent, and only seldom deal with ion pairs of solutes. If the concentration is small enough, average geometry of local structures around ions is quite close to that in the crystalline hydrates and solvates, and one can account for symmetry relations, crystalline bond distances, etc. At extremely high concentrations (up to saturation), however, the concept of local structure has also to be changed. Since by increasing the concentration, the bulk of solvent gradually disappears, ion pair contacts are formed which, in one hand, destroys the original symmetrical hydrate or solvate structures of the solution, and, on the other hand, wide range of moieties, clusters, polymeric species can be formed which may produce a firmly connected network of "solvated salt crystals" within the liquid.

Examples of various extremes of local structures will be presented. Diffraction studies show, e.g., that sodium aluminate solutions [1] contain $Al(OH)_4^-$ ions, surrounded by hydrating molecules and hydrated Na^+ and OH^- ions are swimming in the bulk of water. When concentration increases, various forms of aluminate-Na^+ ion pairs, and dimers or even oligomers of aluminate species are supposed to form.

Interestingly enough, we found [2,3] that high concentrated solutions may exhibit structural units, which has been detected in gas phase mass spectrometric experiments, in completely different extreme circumstances. The clusters detected by these methods were generated from low concentrated lithium halide solutions of acetontirile and methanol and are similar to some local structures formed in high concentrated solutions.
A big pile of experiments and computer simulations shows that in high concentrated aqueous solutions the second hydration shell of ions is destroyed and the counterions will be located nearer to the hydrated ions. This leads to a stepwise formation of solvent separated ion pairs, than contact ion pairs, than more complex structures. The process will be illustrated and each steps will be classified.

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F-I1

Molecular Dynamics of Iron Cations in Water

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Theoretical investigations about the interaction of Fe^{2+} and Fe^{3+} with water date back to more than 25 years and many have appeared in the literature since then. There are different reasons for this interest: The strong nonadditive effects in the interaction of the cations with water; the acidity of its solutions and the reactions related to it; the two different oxidation states that iron ions can assume; the fact that iron, as a transition metal, interacts with its environment in a more complicated way compared to, for example, alkali ions. We review former theoretical investigations and present two new simulation experiments: In the first one we use a newly developed flexible water model (SPC+CCL) in molecular dynamics simulations of solvated Fe^{2+} and Fe^{3+} ions together with an effective ion-water potential. We show that this potential manages to reproduce structural and dynamical properties of the solution. In the second one we used the Car-Parrinello method to study the solvation of a single Fe^{3+} ion, without the use of explicit potential functions, in a box containing 32 water molecules.

F-I2

Electrolyte adsorption in disordered porous material

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Equilibrium properties of the model electrolyte solutions in a disordered environment mimicking a microporous adsorbent were studied. These systems may be considered as partly-quenched[1,2] in which some of degrees of freedom are quenched (adsorbent), and others are annealed and allowed to equilibrate (adsorbate). The ensemble average used to calculate the thermodynamic properties in such systems becomes a double average: first, as usually, over the annealed degrees of freedom, and then over all possible values of the quenched variables. The numerical results of our study follow from the application of the replica Ornstein-Zernike (ROZ) integral equations in the hypernetted chain (HNC) approximation[3-5]. Different electrolyte and matrix models were examined with the parameters mimicking real electrolyte solutions. The effects of the adsorbent porosity and preparation, and the electrolyte and solvent conditions on the chemical potential of adsorbed electrolyte are examined. Confinement has a substantial influence on the properties of adsorbed electrolyte; the mean activity coefficient of the confined electrolyte differs substantially from the same quantity for the corresponding unperturbed solution. Adsorption isotherms are calculated for various conditions and the grand canonical Monte Carlo method is used to asses the validity of replica OZ/HNC theory. The effects of template particles, used in the process of adsorbent „preparation", are examined.

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G-I1

Sulfite solution species by sulfur spectroscopy

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Synchrotron-based sulfur K-edge X-ray absorption near-edge spectroscopy (XANES) has been used to study 50 mM solutions of sodium sulfite at different pH. The sulfur species display unique features at the absorption edge in the XANES spectra, corresponding to electron transitions S(1s) to antibonding molecular orbitals of π-character. The position and splitting of the peaks in the experimental spectrum of the SO_2 molecule have been reproduced by Density Functional Theory calculations (DFT), and assigned to electronic transitions. At low pH (<2) the XANES spectra show that the hydrated sulphur dioxide molecule, $SO_2(aq)$, dominates in the acid solution. The concentration of the sulfurous acid molecule, $H_2SO_3(aq)$, responsible for the acidity, is below detection limit. In the intermediate pH range, $2 < pH < 7$, the spectra show comparable amounts of two hydrogen sulphite species, HSO_3^- and SO_3H^-, with the hydrogen atom coordinated to the sulfur and oxygen atoms, respectively. With increasing temperature, from 4 to 70 °C, the spectra show an increasing amount of the minor HSO_3^- species. XANES spectra and neutron powder diffraction on solid $CsDSO_3$ confirm a pyramidal structure with an S-D distance of 1.38 Å, consistent with the solution structure of HSO_3^-. Vibrational spectra have been recorded and assigned. The results show that sulfur K-edge XANES spectroscopy has become a powerful analytical tool for this "spectroscopically silent" element, and also that the electronic transitions near the sulfur K-edge can be used to probe the local coordination geometry in great detail.

G-I2

Micelle Hydration and Dynamics in Aqueous SDS Solutions

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Dielectric spectra have been measured for aqueous sodium dodecylsulfate (SDS) solutions up to 0.1 mol L-1 at 25 °C over the frequency range $0.005 \leq \nu$ / GHz ≤ 89. The spectra exhibit two relaxation processes at *ca.* 0.03 GHz and 0.2 GHz associated with the presence of micelles in addition to the dominant solvent relaxation process at *ca.* 18 GHz and a small contribution at *ca.* 1.8 GHz due to H_2O molecules hydrating the micelles.

Detailed analysis reveals that the micelles bind 20 water molecules per SDS unit, but not as strongly as trimethylalkylammonium halide surfactants do. The relaxation times and amplitudes of both micelle relaxation processes can be simultaneously analysed with the theory of Grosse, yielding the effective volume of a SDS unit in the micelle and the lateral diffusion coefficient of the bound counter ions. The findings of this investigation fully corroborate recent molecular dynamics simulations on structure and dynamics of SDS micelles.

Oral presentations

A1

Structure determination of some ruthenium and iron complexes by X-ray diffraction

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The structure of $[Ru(bpy)(CN)_4]^{2-}$ (byp-bypiridine) and $[Fe(dmdt)]^{2+}$ (dmdt-diacetylmonoximdietylentriamine) complexes have been investigated by X-ray diffraction technique in aqueous and methanol solutions respectively.

The $[Ru(bpy)(CN)_4]^{2-}$complex having only one chromophoric ligand is considered as the simplest molecule within the class of ruthenium(II) polypyridine photosenzitizers of excellent spectroscopic, photophysical, photochemical and electrochemical properties for conversion and storage of solar energy and as a unit of polynuclear and supramolecular species in which the centers of metal complexes or other type of molecules are bridged by cyanide ligands. The characteristic bond lengths of the complex obtained by this method are in good agreement with those determined by single-crystal X-ray study. The number of solvent molecules of the hydration shell has been determined. Three water molecules are arranged near to each cyanide ligands. The average distance between the nitrogen atom of cyanides and the oxygen atom of these solvent molecules is found to be 3.2 Å.

The oxidation of pyrochatechine and its derivatives in living cells is one of the main functions of the copper and iron containing oxidoreductases, so there is important to know the structure of $[Fe(dmdt)]^{2+}$ tip complexes. Since there is not possible to determine the single crystal structure of the complex we have tried to examine it in solution. The structure of 1M methanol solution of $[Fe(dmdt)]^{2+}$ complex was determined from X-ray diffraction measurement.

A2

Conformational Change of Solvent *N,N*-Dimethylpropionamide upon Coordination to the Manganese(II) Ion

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Molecular structure of solvent remains usually unchanged, even if strong steric hindrance operates among solvent molecules bound to the metal ion. Indeed, 1,1,3,3-tetramethylurea (TMU) coordinates to the manganese(II) ion without appreciable change in its molecular structure. However, recently, we found an interesting solvent *N,N*-dimethylpropionamide (DMPA), which changes its conformation upon coordination to the metal ion. Thermodynamic and spectroscopic evidence on the conformational change of DMPA will be presented here, and the results will be discussed from the view-point of solvation steric effect.

It elucidates that a series of mono-, di-, tri- and tetra-bromo complexes of manganese(II) are formed in DMPA, as well as TMU. Formation of the mono-bromo complex is strongly enhanced, almost to the same extent in these solvents, over that in DMF, suggesting that significant solvation steric effect operates in both solvents. This is expected because the manganese(II) ion is five-coordinated in both the solvents. However, a significant difference was found for the formation enthalpy of $MnBr^+$, *i.e.*, it is exothermic in TMU, while endothermic in DMPA (Fig. 1). The difference can be well explained in terms of conformational geometry change of DMPA from *planar cis* to *non-planar staggered* with the C-C-C-O dihedral angles of 0° and 90°, respectively.[1] The *non-planar staggered* predominates in the $Mn(DMPA)_5^{2+}$, while the *planar cis* is preferred in the $MnBr^+$ complex.. The transition from the *non-planar staggered* to *planar cis* is thus associated with the formation of $MnBr^+$. This is supported by titration Raman spectroscopy with regard to the $MnBr^+$, which is four-solvated in DMPA, and also by the enthalpies of transfer of $MnBr_n^{(2-n)+}$ (n = 0-4) from TMU to DMPA.

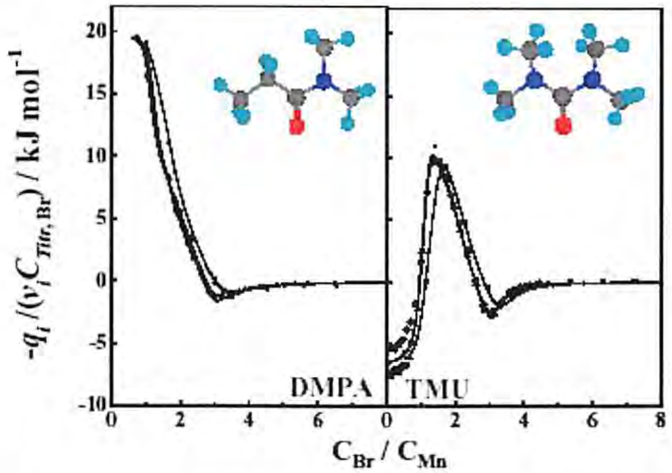

Fig.1. Calorimetric titration curves for the Mn^{2+}-Br^- system in DMPA and TMU at 298 K.

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A3

Kinetics and mechanism of formation and decomposition of $(CN)_5Pt{-}Tl(edta)^{4-}$

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Chemistry of platinum–thallium cyano compounds containing a direct and unsupported by ligands metal–metal bond is in the middle of interest of our group. Detailed studies of the structures and the unusual equilibria has already been reported. Formation kinetics of the following reaction has been showed at the DD4 – IRM meeting 2002 in Kloster Banz:

$$Pt(CN)_4^{2-} + Tl(CN)_4^{-} \rightleftharpoons [(CN)_5Pt{-}Tl(CN)_3]^{3-} \qquad (1)$$

Research on substitution of the cyanides bonded to Tl with amino–polycarboxylates (e.g. $mimda^{2-}$, nta^{3-}, $edta^{4-}$) is under progress in our laboratories. This poster is to show our results on the formation kinetics of the complex $[(CN)_5Pt{-}Tl(edta)]^{4-}$. The overall reaction of the formation ($K_{eq} = 20 \pm 2$) is:

$$Pt(CN)_4^{2-} + Tl(edta)(CN)^{2-} \rightleftharpoons [(CN)_5Pt{-}Tl(edta)]^{4-} \qquad (2)$$

The complex can form from $(CN)_5Pt{-}Tl$ with the reaction of edta. This reaction yields 100 % $[(CN)_5Pt{-}Tl(edta)]^{4-}$, which slowly decomposes corresponding to the chemical equilibria of reaction (2). If the concentration of $[(CN)_5Pt{-}Tl(edta)]^{4-}$is low enough then the decomposition is irreversible and possible to determine the rate separately.

I, Even though the concentration of $Tl(CN)_4^{-}$ is 4 orders of magnitude lower than the $[Tl(edta)(CN)^{2-}]$ in the reactant, the formation of $[(CN)_5Pt{-}Tl(CN)_3]^{3-}$ is much faster than the one of $[(CN)_5Pt{-}Tl(edta)]^{4-}$. Therefore a path, where $[(CN)_5Pt{-}Tl(CN)_3]^{3-}$ is an intermediate and the substitution of the cyanides on the Tl side with edta leads to the product, is proposed:

(a) $Pt(CN)_4^{2-} + Tl(CN)_4^{-} \rightleftharpoons [(CN)_5Pt{-}Tl(CN)_3]^{3-}$ / $k_1;k_{-1}$
(b) $[(CN)_5Pt{-}Tl(CN)_3]^{3-} \rightleftharpoons [(CN)_5Pt{-}Tl(CN)_2]^{2-} + CN^-$ / $k_2;k_{-2}$
(c) $[(CN)_5Pt{-}Tl(CN)_2]^{2-} + H_xedta^{(4-x)-} \rightleftharpoons [(CN)_5Pt{-}Tl(edta)]^{4-} + 2CN^- + xH^+$ / $k_3;k_{-3}$

II, However under appropriate conditions (where the concentration of $Tl(CN)_4^{-}$ is suppressed with excess edta) an other path, where $Pt(CN)_4^{2-}$ reacts directly with $Tl(edta)(CN)^{2-}$, can dominate.

(a`) $Pt(CN)_4^{2-} + Tl(edta)(CN)^{2-} \rightleftharpoons [(CN)_4Pt\cdots Tl(CN)(edta)]^{4-}$ / $k_{1'};k_{-1'}$
(b`) $[(CN)_4Pt\cdots Tl(CN)(edta)]^{4-} + CN^- \rightleftharpoons [(CN)_5Pt\cdots Tl(CN)(edta)]^{5-}$ / $k_{2'};k_{-2'}$
(c`) $[(CN)_5Pt\cdots Tl(CN)(edta)]^{5-} \rightleftharpoons [(CN)_5Pt{-}Tl(edta)]^{4-} + CN^-$ / $k_{3'};k_{-3'}$

Provided that all intermediates are in steady state, standard derivation yields the following expression for $k_{obs} = 1/\,[Pt(CN)_4^{2-}] \cdot d[(CN)_5Pt{-}Tl(edta)^{4-}]/dt$:

$$k_{obs.} = \frac{k_1 \cdot k_2 \cdot k_3 \cdot [edta] \cdot [Tl(CN)_4^-] + k_{-1} \cdot k_{-2} \cdot k_{-3} \cdot [CN^-]^3}{k_{-1} \cdot k_{-2} \cdot [CN^-] + k_1 \cdot k_3 \cdot [edta] + k_2 \cdot k_3 \cdot [edta]} + \frac{(k_{1'} \cdot k_{2'} \cdot k_{3'} \cdot [Tl(CN)(eda)^{2-}] + k_{-1'} \cdot k_{-2'} \cdot k_{-3'}) \cdot [CN^-]}{k_{-1'} \cdot k_{-2'} + k_{-1'} \cdot k_{3'} + k_{2'} \cdot k_{3'} \cdot [CN^-]}$$

This model fits to the observed data.

A4

Analysis of the thermodynamic and structure data internal consistency for binary liquid alkali-metal mutual solutions

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The thermodynamic analysis of the above solutions has been made in our presentation on 27th ICSC (Vaals) in the terms of the long-wavelength limit of the correlation function of concentration fluctuations $S_{cc}(0)$. The function $S_{cc}(0)$ proved to be an efficient instrument for analysis of the thermodynamic properties behaviour peculiarities of these solutions particularly for estimation of the concentration fluctuations magnitude and stability of the solution as a single-phase homogeneous system. Now an application of this function for analysis of the thermodynamic and structure properties internal consistency is discussed.

Function $S_{cc}(0)$ is unambiguously linked with the long-wavelength limit of the structure factor $S(0)$, which is determined in diffraction experiment with small-angle scattering of the X-rays or neutrons (small-angle limit): $S(0)=\frac{\langle f\rangle^2}{\langle f^2\rangle}\left[\left(\delta-\frac{f_1-f_2}{\langle f\rangle}\right)^2\cdot S_{cc}(0)+\frac{\beta_T\cdot RT}{v}\right]$. In formula: $\langle f\rangle=x_1f_1+x_2f_2$, f_i is a long-wavelength limit (wave vector q=0) of the atomic scattering factor for atom i; $\langle f^2\rangle=x_1f_1^2+x_2f_2^2$; v is the molar volume; $\delta=(1/v)(\partial v/\partial x_2)_{p,T}$ is the dilatation factor; x_2 is the molar concentration of the light component; $\beta_T=-(1/v)(\partial v/\partial p)_{T,x_i}$ is the isothermal compressibility of the solution. $S(q)$ is normalized through its division by $\langle f^2(q)\rangle$.

Thus, $S_{cc}(0)$ is a structure-sensitive quantity. It can be determined using independent thermodynamic and diffraction experiments and hence it serves as an criterion of thermodynamic and structure properties internal consistency. The binary alkali metal systems Cs-Na, K-Na, Cs-K are taken as a model using the obtained experimental data at T=400-1200K in the entire range of x_2.

Acknowledgements

The authors are grateful to the Russian Foundation for Basic Research (grant 02-02-16175).

Old and New about the Hydroxide Ion in Aqueous Solution

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ABSTRACT

During the last decade there has been an enhanced interest in investigating the nature and transport phenomenon of hydroxide ion in aqueous solutions. A large number of theoretical tools ranging from the high level quantum mechanical methods to the most recent Care-Parinello molecular dynamics have been applied. These efforts have resulted in novel insights into the structural properties, energetics, vibrational frequencies and transport mechanism of OH^- ion in water. At present relatively few experimental studies exist in the literature. However, guided by the theoretical results some progress in this front has also been made very recently. Thus, a review in this field is both timely and important. After a thorough survey and analysis of the existing literature regarding the state of hydroxide ion in aqueous solutions, special emphasis will be given to the nature of blue shifts seen in the O-H streching vibrational frequency in clusters by MD simulations or in experiments. The results obtained by cluster studies will be analysed with respect to the optimal cluster structures, energetics and the dependence of cluster properties on the nature of computational method. Structural and dynamical properties of alkaline solutions obtained by classical or by ab-initio simulation methods will be analysed and compared with the results of these cluster studies. Results from our own quantum chemical calculations and MD simulations will be presented and the direction of future work in this area will be discussed.

A6

VOLUMETRIC AND THERMAL PROPERTIES OF SOME AQUEOUS ELECTROLYTE SOLUTIONS.

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The volume-concentration relations in electrolyte solutions are less known when the temperature dependence of properties is considered. Therefore, precise densities of 0.1, 0.5 and 1.0 mol·kg^{-1} aqueous solutions of lithium nitrate, lithium carbonate, sodium iodide, sodium nitrate, sodium acetate, sodium carbonate sodium sulfate, potassium bromide and potassium iodide were determined at 1K temperature intervals from T = 277.15 K to T = 343.15 K. Measured densities ρ(T;m) were expressed as polynomials of temperature and these polynomials were used in the calculation of the apparent molar volumes at constant molality m, $V_{2,\Phi}$, the coefficients of thermal expansion, α(T;m), the apparent molar expansibilities, $V_{2,E}$ and by applying the Maxwell relationship, the changes of molar heat capacity with pressure.

$$V_{2\Phi}(T;m) = \frac{M}{\rho} + \frac{1000(\rho - \rho_w)}{\rho \rho_w}$$

$$\alpha(T;m) = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,m}$$

$$V_{2E}(T;m) = \left(\frac{\partial V_{2\Phi}(T;m)}{\partial T}\right)_{P,m}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,m} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,m} = -T\left(\frac{M}{\rho}\right)\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_{P,m}\right]$$

where ρ_w is the density of pure water and M is the molar mass of dissolved salt.

The obtained results are compared with the literature data and discussed with regard to the ion-water and ion-ion interactions.

A7

Excess Molar Properties of Binary Mixtures of Epichlorohydrin with Toluene and Xylene and Benzene at Different Temperatures

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Epichlorohydrin is a useful substance and has the potential for use in organic processes (1). In this study, excess molar volumes, V^E, have been calculated from measured values of density over the whole composition range at the temperatures 298.15, 303.15 and 308.15 K for the mixtures epichlorohydrin + (toluene, or xylene). The results are discussed in term of the molecular and other intermolecular associations.

Excess molar volumes of these binary mixtures were calculated from the corresponding density measurements using the relation (2):

$$V^E = \frac{(1-x)M_1 + M_2X}{\rho_m} - \left(\frac{(1-x)M_1}{\rho_1} + \frac{XM_2}{\rho_2}\right) \qquad (1)$$

The experimental excess molar volumes for these mixtures at various mole fractions and at 298.15, 303.15 and 308.15 K were fitted by the method of least squares to the Redlich-Kister equation of the form (3):

$$V^E = X_1X_2\sum_{i-1}^{n} a_j (X1 - X2)^{i-1} \qquad (2)$$

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A8

Excess Molar Volumes and Viscosities for Binary Mixtures of Alkoxyethanols with Substituted and Cyclic Amides at 298.15K

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The study of the effect of simultaneous presence of ether(-o-) and (-OH) groups on the excess thermodynamic properties and the corresponding behaviour of alkoxyethanols in binary mixtures is of great relevance in understanding the nature of the interactions. The excess molar volumes and viscosities have been measured as a function of composition for binary mixtures of N,N-dimethylformamide, N,N-dimethylacetamide, 2-pyrrolidinone, and N-methyl-2-pyrrolidinone at 298.15K. In all mixtures the excess molar volumes are negative over the whole mole fraction range. From the experimental data, deviation in the viscosities have been calculated. The effect of the specific interaction on the excess properties, dependence on the position of methyl group in 2-propoxyethanol and 2-isopropoxyethanol and the influence of N,N-disubstituted and cyclic amides have been discussed. The results have also been confirmed through our IR studies.

A9

Volumetric and thermal properties of some electrolyte solutions

Emanuel Manzurola

Abstract not recieved.

A10

Photooxidation of water by 2,6-dichloro-1,4-benzoquinone

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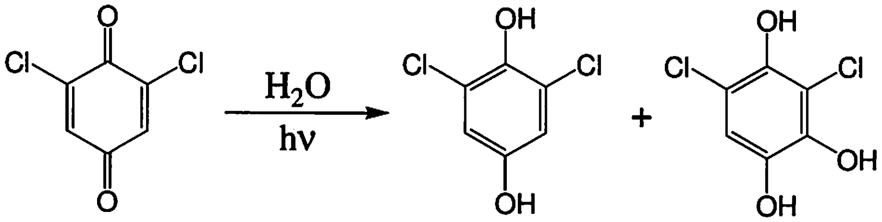
Our recent studies on the catalytic oxidation of chlorophenols revealed that these reactions are sensitive to visible light, which was explained by the photoreactions of chloroquinone intermediates.[1] The poster will summarize our results on the most important relevant photoreaction, the aqueous photoreduction of 2,6-dichloro-1,4-benzoquinone:



No hydrogen peroxide was detected in the final aqueous solution but an increase in the dissolved oxygen concentration indicated that water is oxidized to molecular oxygen. The reaction is driven efficiently by visible light, which is absorbed by 2,6-dichloro-1,4-benzoquinone. Our studies on the kinetics and mechanism of the photoreaction will be discussed and the findings will be compared to results obtained with different quinones using UV irradiation.[2,3]

This research was supported by the Center for Catalysis, Institute for Physical Research and Technology, Iowa State University. GL also wishes to thank the Fulbright Program.

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A11

THE INFLUENCE OF CO_2 ON THE SOLUBILITY OF AMORPHOUS SODIUM DISILICATE

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ABSTRACT

Sodium silicates belong to family of soluble silicates, known also as waterglasses, that represent one of the most versatile inorganic chemicals available. Sodium silicates are manufactured by melting a mixture of soda and quartz sand; the resulting products are anhydrous, amorphous waterglass lumps. The dissolution of these lumps in an autoclave yields the aqueous sodium silicate solution. By spray drying of this solution, a hydrated amorphous powder, easily soluble in water is obtained. The most common product of dried waterglas is sodium disilicate, $Na_2O.2SiO_2$, commercially known as NADIS. It is important for detergent industry, where it plays a multifunctional role. One of the most important quality parameters of NADIS is its solubility, where the insoluble residue on filter paper is being measured after a weighed quantity of sample is placed in water for 10 minutes. The analyses of NADIS, produced in a directly-heated spray dryer, showed great variabilities of insoluble contents of the product. We ascertained that the reason for such a versatility of solubilites was closely connected to a CO_2 content of NADIS samples.

The aim of our research was the comparison of two samples of NADIS, having different contents of CO_2 (0.4 and 9.5%), with regard to their structural properties and physico-chemical behavior, with special emphasis on solubility. We will try to clarify the connection between CO_2 content of NADIS and its influence on product's solubility.

A12

REGULAR STRUCTURE CHANGE OF LIQUIDS ON LIQUID-LIQUID MIXING DUE TO EXISTENCE OF MICROSCOPIC MOLECULAR GROUPS

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Structure changes of liquids on liquid-liquid mixing have been studied by X-ray diffraction method. Acetonitrile(AN), acetone(AC), pyridine(Py), benzene(Bz), and water(H_2O) were used as the liquids. X-ray diffraction measurements have been carried out at 25°C for the neat liquids and AN-H_2O, AC-H_2O, Py-H_2O, AN-AC, and Bz-Py mixtures of various mixing ratios. Radial distribution functions (RDFs) were obtained and compared with those calculated by assuming the additivity of structures of neat liquids in each binary system. The differences between observed and calculated RDFs in each system except the Bz-Py system revealed almost the same pattern independent of the mixing ratio; the differences in the Bz-Py system were very slight. This result could be interpreted by assuming that the liquid molecules form microscopic molecular groups which are classified into three kinds of molecular groups having different structures. The structures of the first and the second molecular groups are the same as those of neat liquids and the third molecular group has a definite structure formed by the interactions between different liquid molecules. When we denote the radial distribution functions representing these structures in the binary system of A and B as $D_A(r)$, $D_B(r)$, and $D_{AB}(r)$, respectively, the difference RDF denoted as $\Delta D(r)$ can be expressed by

$$\Delta D(r)=\Delta f_A\{D_{AB}(r)-D_A(r)\}+\Delta f_B\{D_{AB}(r)-D_B(r)\}$$

where Δf_A and Δf_B are the volume fractions of A and B molecules existing in the third molecular groups, respectively, and the ratio of Δf_A and Δf_B is presumed to be constant. The maximum of Δf_A or Δf_B gives that of $\Delta D(r)$ which was observed at $x_{AN}=0.3$ ($f_{AN}=0.5$-0.6), $x_{AC}=0.2$ ($f_{AC}=0.5$), $x_{Py}=0.3$ ($f_{Py}=0.6$-0.7), and $x_{AN}=0.6$ ($f_{AN}=0.5$) for AN-H_2O, AC-H_2O, Py-H_2O, and AN-AC systems, respectively, where x_A and f_A are the mole fraction and volume fraction of A, respectively. These values of mole fraction or volume fraction are close to those giving the maximum of excess density corresponding to the deviation from the additivity of densities of liquids A and B. The present study has clarified that the molecular groups of A and those of B exist still in the liquid mixtures although the A and B molecules form new molecular groups having a definite structure. Each molecular group probably behaves like a flickering cluster having no definite size.

A13

Aqueous solution studies on copper(ii) / fluoroquinolone complexes

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Quinolones are a family of drugs widely used as antimicrobial agents and exert their action by inhibiting DNA synthesis. Although , the intracellular targets by which these compounds mediate their effects is still a matter of investigation it was postulated that the mechanism of action is due to cooperative binding of quinolone to DNA required to inhibit DNA gyrase and that it could be mediated by transition metal ions. As an attempt to clarify the role of transition metals and how they exert their action on biological systems, the coordination behavior of the systems Cu(II)/norfloxacin and Cu(II)/ofloxacin, in aqueous solution, has been studied. The equilibrium constants of the systems Cu(II)/norfloxacin/phenantroline and Cu(II)/ofloxacin/phenantroline have also been determined by potenciometry under an argon atmosphere at 25.0±0.1 °C, and the ionic strength was adjusted to 0.1 *M* with sodium chloride. All the calculations were performed with program HYPERQUAD.

The values obtained for the acidity constants of ofloxacin, norfloxacin and 1,10-phenantroline and the stability constants with copper(II) were determined and the model used to determine the stability constants of the ternary systems was:

$$Cu^{2+} + HL^{\pm} + L_1 \Leftrightarrow [CuHLL_1]^+ \qquad \beta_{1110}$$
$$Cu^{2+} + HL^{\pm} + L_1 \Leftrightarrow CuLL_1 + H^+ \qquad \beta_{111\text{-}1}$$

where HL is the fluoroquinolone in its zwiterionic form and L_1 phenantroline in its neutral form. The values obtained show that the ternary complexes are much more stable than expected and that the interactions ofloxacin/phenantroline and norfloxacin/phenantroline must be mediated by the copper (II) cation.

A14

Catalytic Behaviour of Rhodium-Phosphatriaza-Adamantane Complexes

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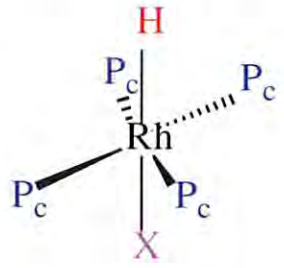
Since the discovery of the water-soluble phosphine complexes of rhodium they play an important role in the aqueous phase catalytic processes both is laboratry and in industrial scale. In these systems water can never be regarded as a simple solvent: doe to its basicity (or acidity) it can be greatly influence the characterystic of a reaction.[1,2]

In the literature several papers deal with the effect of the pH of the aqueous solution on the distribution of the catalytically active species which might directly affect the selectivity. Now we present our results in the 1,3,5-triaza-7-phosphaadamantane (PTA) /rhodium system. As a function of pH and hydrogen pressure dihydride and monohidride can be identified from the ^1H and ^{31}P spectra which results were confirmed by acid-base titration. The monohydrido-rhodium complex is stable only at pH>10 and was active in hydrogenation of acetophenon to phenyl-ethanol. The dihydrides formed in the range of 2<pH<10 in our system, can be regarded as active species of hydrogenation of olefines.



$[RhH(PTA)_4X]$

Acknowledgement

The authors thank for the support of the following grants: FKFP, Hungary, A/K 813/0183 (L.N.), OTKA, Hungary, T029934 (F.J). and F037358 (J.K.).

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A15

Ion-Pair Formation of 2,2-Electrolytes in Water from Electric Conductivity Measurements

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Investigations on the temperature and concentration dependence of electric conductivity of electrolytes belong to the most precise methods yielding information on ion-ion and ion-solvent interaction. Whereas systematic studies of 1,1-electrolytes in many solvents have been reported[1-3] less attention has been paid to the temperature dependence of conductivity of 2,2-electrolytes[4].

In this work electric conductivities of diluted solutions of aqueous cobalt, nickel, copper and zinc sulfate solutions were measured from 5 to 35° C. The measurements on solution conductivity were carried out on highly pure products and in an inert atmosphere with an equipment yield precise data.

The Fuoss-Justice equation for associated electrolytes based on the low concentration chemical model[5] of electrolyte solutions is applied to yield the limiting conductivities and association constants. From the temperature-dependent Gibbs energy of ion-pair formation the entropy and enthalpy of the association process are available. The comparison between the thermodynamic data of ion-pair formation of 2,2-electrolytes in water from heat of dilution measurements[6] will be given.

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A16

Small-angle neutron scattering study of aqueous solutions of 1,2 hexanediol

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Long chain alcohols with two or more OH groups are known to behave similarly to conventional surfactants in aqueous solutions, for instance above some critical concentration they form micelle-like aggregates [1,2]. We studied heavy water solutions of 1,2- hexanediol by means of small-angle neutron scattering (SANS) at the YuMO time of flight spectrometer at the JINR (Dubna), in the alcohol mole fraction range 0.01 – 0.20. The experimental scattering data allowed the analysis using two approaches: the traditional one, when the scattering is attributed to the presence of micelles [2], and an alternative one, based on the Bhatia–Thornton formalism [3]. There, the zero-angle limit of the scattered intensity, I(0), is proportional to the particle number and concentration fluctuations in the mixture. Using the experimental I(0) together with some thermodynamic data, useful quantitative measures of the aggregation behavior in the mixtures could be evaluated such as the concentration fluctuations and the Kirkwood-Buff integrals [4]. The behavior of 1,2-hexanediol and the similar 2-butoxyethanol solutions will compared.

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A17

Structure of new heterometallic Ru/Cu, Ni complexes in water solution and hexane by XAFS spectroscopy

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The recovery of platinum group metals from the high level radioactive solution is operable to eliminate destabilizing action of these metals in the vitrification of wastes. Effective extraction of nitro-nitrozo-hydroxo Ru anions by trialkylphosphine oxide to hexane has been revealed recently in a presence of transition metal cations only. This phenomenon could be explained by a formation of heterometallic complexes in organic solvent. The goal of the present work is to study a local environment geometry of Ru and a structure of Cu, Ni cations environment both existing in aqua solutions and hexane extracts.

The analysis of the EXAFS and XANES spectra of the aqueous solutions and hexane extracts shows that the interaction between hydrated (or solvated by the trioctylphosphine oxide molecules) Cu(II), Ni(II) cations and the complex Ru anion takes place. This interaction is accompanied by the increase of the interatomic distances Ru–O from 1.96 Å to 1.99 Å. Structural models have been proposed for heterometallic complexes of several types. Rigid chemical binding between Ru- and Cu, Ni- fragments of heterometallic complex in aqua solution and hexane extracts was established. This binding existence explains the effective extraction of Ru-containing anions with transition metal cations. The interatomic distances Cu-Ru and Ni-Ru are estimated at 3.4 Å and 2.7 Å, correspondingly. Such rigid binding can be provided by double chemical bonding by two ligands of Ru fragment, in accordance with conclusions concerning structure of "mixed" Ru/Cu, Ni complexes in extracts, obtained recently by IR and electron spectroscopy [1].

Financial support from the RBRF (Project 03-03-32354) is greatly appreciated.

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A18

NMR study on some metal O,O'-dialkyldithiophosphates

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In a current project, we are aiming to reach a better understanding of the surface complexation during mineral froth flotation. To this end we are currently preparing samples of pure minerals and collectors, to be studied using solid-state NMR techniques. However, the spectra of these samples are often quite complex and the low concentration of ligands in the mineral-collector samples often lead to weak signals. Therefore, we have recognized the need for model systems giving spectral data that can facilitate the interpretation of the surface-complex spectra.

Complexes of Zn(II), Cd(II), and Pb(II) and various O,O'-dialkyldithiophosphates have been prepared from water solution, and re-crystallized from suitable organic solvents. These complexes have been studied using ^{31}P- and ^{13}C NMR in solid state (CP/MAS and direct polarization) as well as in solution at different concentrations. Combining the information (isotropic chemical shift and CSA) given by liquid-state and solid-state spectra of the model systems, it is possible to distinguish between chelating and bridging ligands, thus providing a tool for unveiling the nature of the interaction between collector and mineral surface.

Acknowledgement

We are indepted to Cheminova A/S for supplying di-O-alkyldithiophosphates, ARC for financial support, and to The Swedish Research Council for funding of the CMX-360 NMR spectrometer.

A19

INFRARED, RAMAN AND THEORETICAL STUDIES OF METAL-OXYGEN BONDING OF COMPLEXES EXISTING IN SOLUTIONS

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Metal ions have a great tendency to form complexes with water molecules and ligands with oxygen donors. The study of structure and bonding of aqua complexes is always a difficult task in solution. Infrared and Raman spectroscopy with combination of EXAFS (extended X-ray absorption fine structure spectroscopy) and LAXS (large-angle X-ray scattering) can be used for studies of symmetry and bonding properties.

Spectroscopic and theoretical study of halide and pseudohalide complexes of general composition $[TlX_n(OH_2)_m]^{(3-n)+}$, X=Cl,Br, CN[1], $M(OH_2)_6^{n+}$ (M=Al, Ga, In, Tl, Ti, V, Cr, Fe, Co, Ru, Ir, Hg)[2], triflate aqua complexes, $[Hg(OH_2)_2(CF_3SO_3)_2]_\infty$, $[Tl(OH_2)_3(CF_3SO)_3]$[3], dmso complexes of $M(dmso)_6^{3+}$ (M = Al, Ga, In, Tl, Sc, Y, La, Ru) [4] have been performed. A special attention has been paid to the metal-oxygen vibrational modes. Due to our broad variety of complexes we were able to obtain a general correlation between bond distances and stretching force constants (Fig. 1). Particular but much better correlation's have been observed for complexes of homologue series. Other structurally important parameters like coordination numbers and symmetry (point groups) of the complexes have been established.

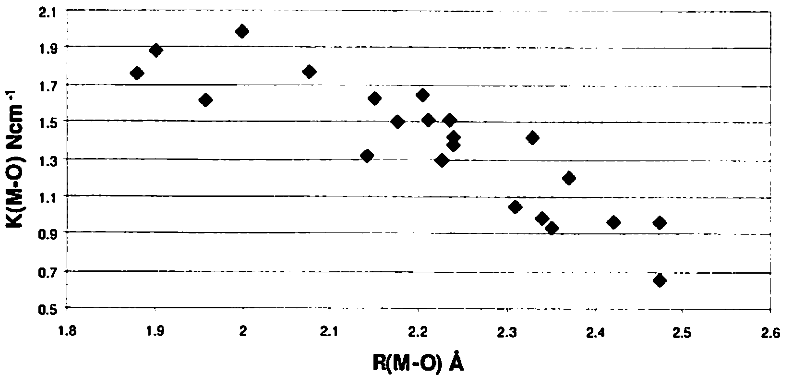

Fig. 1. Correlation between M-O bond distances (R) and stretching force constants (K)

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A20

Structural analysis of Al-EDTA complexes in aquous solution by means of NMR and X-ray absorption spectra

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Though hydrated Al ion has strong toxicity in soil, its toxicity decreases by the complex formation with natural organic compounds which mainly possesses carboxyl groups. Therefore, it is important for environmental sciences to clarify the structure between Al and natural organic compounds under the molecular level(1). We have employed EDTA(ethylenediaminetetraacetate) as a model compound of natural organic compounds, and clarified the structure of Al-EDTA complexes in aquous solution. By our NMR study, we could show that Al atom of Al-EDTA complex in aquous solution has 5-fold coordinated structure with one O atom of an H_2O molecule, two N atoms of an EDTA molecule, and two O atoms of the CH_2COO groups in an EDTA molecule(2). However, as the steric structure was not clear from the NMR study, we have analysed the structure by means of X-ray absorption spectra. As a result, we have proved that the Al-EDTA complex in aquous solution has two structures of trigonal bipyramidal and square pyramidal structures with their ratio of 7:3. And we have investigated the existence of 4-fold coordinated complex in solution by further NMR study. When it was low temperature, the NMR peak of 4-fold coordination at 60~70 ppm grew up. The detail discussion will be reported at the conference.

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A21

Dielectric Relaxation Spectroscopy of Aqueous Hexyltrimethylammonium Bromide Solutions

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Dielectric permittivity measurements of aqueous hexyltrimethylammonium bromide solutions are done as function of concentration ($0.04 \leq m$/mol kg-1 ≤ 1.0) covering the frequency range of $0.2 \leq$ □/GHz ≤ 89 at 298.15 K. In order to obtain the enthalpy and entropy of activation, temperature dependence measurements are done for two solutions (0.25 and 0.76 mol kg-1) in the range of $278.15 \leq T/\mathrm{K} \leq 338.15$. All the spectra are described by a superposition of four individual Debye relaxation processes in the entire range of concentration and temperature. The low frequency dispersion step, centered at 1 GHz is attributed to the tumbling motion of solvent-separated (SSIP) ion pairs. The equilibrium constant, K_A of the ion pair deduced from the ion pair dispersion amplitude is 45 ± 1. The remaining three relaxation processes with relaxation times, ≈ 25, 9 and 1 are attributed to the water molecules in the vicinity of the hydrophobic tail of hexyltrimethylammonium ion, the cooperative relaxation of H-bond network of bulk water and the fast mobile water molecules respectively. From the analysis of the solvent amplitudes, the hydrophobic hydration number, $Z_s(0) = 9.5 \pm 0.5$ and the number of irrotationally bound water molecules, $Z_{ib}(0) = 5.3 \pm 0.2$ are estimated. From the enthalpy of activation of bulk solvent relaxation process, the average number of hydrogen bonds per water molecule is estimated to be 2.3 ± 0.1, which is slightly lower compared to pure water. The possibility of micelle relaxation process will be discussed.

A22

THERMODYNAMICS OF TRANSFER OF IONS FROM WATER TO AQUEOUS-ORGANIC MIXTURES

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Data on the thermodynamics of transfer of simple electrolytes from water to aqueous-organic mixtures have been collected systematically from the literature and critically reviewed in recent years. Extensive data sets for Gibbs energies, enthalpies and entropies of transfer have been established for co-solvents including MeOH, EtOH, t-BuOH, MeCN and DMSO, with more limited values for other aqueous-organic mixtures. These data were divided, wherever possible, into their component ionic contributions using the tetraphenylarsonium (or phosphonium) teraphenylborate extrathermodynamic assumption. The single ion thermodynamic properties so obtained often exhibit very complex behaviour as the solvent composition changes, especially the enthalpies and entropies. There are marked differences between aqueous mixtures with protic and dipolar aprotic co-solvents, and between cations and anions. Some aqueous-organic mixtures show clear evidence of solvent microheterogeneity. In others there is marked compensation between the enthalpies and entropies or between cations and anions. The behaviour of classes of ions and groups of solvents is discussed in terms of the specific interactions occurring.

A23

Raman spectroscopic study on the solvent conformational change upon solvation to metal ion

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Metal ion solvation is quite important to understand its reaction in solution. Indeed, the solvation number of the metal ion in a bulky non-aqueous solvent is reduced when a strong steric repulsion operates among solvent molecules (*strong solvation steric effect*). Even in the case that the solvation number is not reduced, the coordination geometry around the metal ion is significantly distorted (*weak solvation steric effect*). We have so far investigated the *solvation steric effect* from thermodynamic and structural point of view. The halogeno complexation is enhanced in Hexamethylphosphorictriamide (HMPA), 1,1,3,3-tetramethylurea (TMU) and *N*,*N*-dimethylacetamide (DMA) over *N*,*N*-dimethylform- amide (DMF), despite that the electron-pair donating ability of these solvents are higher than DMF. HMPA and TMU shows a typical *strong solvation steric effect*, *i.e.*, a series of first transition metal(II) ions have all reduced solvation numbers in these solvents. On the other hand, DMA shows a *weak solvation steric effect*, *i.e.*, an octahedral six-coordination is kept unchanged for a series of first transition metal(II) ions, except for the zinc(II) ion, although the coordination geometry around the metal ion and the intermolecular structure of DMA are significantly distorted.

Recently, we developed titration Raman spectroscopy and applied it to elucidate a *steric preferential solvation* of metal ion in DMF-DMA mixture.(1), (2) Further investigation was carried out with *N*,*N*-dimethylpropionamide (DMPA). It is generally accepted that the methyl carbon and oxygen atoms in the DMPA propionyl group CH_3CH_2CO- locate on the amide plane and at the *cis* position with each other. However, Raman spectra of DMPA solution measured at varying temperature indicate the presence of another isomer in equilibrium with the *cis* form. DFT calculations show that the *non-planar staggered* form with 92° C-C-C=O dihedral angle is slightly unstable than the *cis* form in both the gas phase and SCRF solution.(3) Interestingly, we also found that the isomerization enthalpy of DMPA solvated to metal ion strongly depends on the metal ion. Here, we will demonstrate our experimental and theoretical evidence for the presence of conformational equilibria of DMPA in the balk and in the solvation sphere of the metal ion.

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A24

Specific Cation Effect on Quenching Reactions of Excited Tris(2,2'-diimine)ruthenium(II) and Tris(2,2'-bipyridine)chromium(III) by Negatively Charged Complexes in Aqueous Solutions

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Specific salt effects were studied on the quenching reaction of excited Tris(2,2'-diimine)ruthenium(II) and Tris(2,2'-bipyridine)chromium(III) by various negatively charged complexes in aqueous solutions as a function of alkali metal ions which were added for adjustment of ionic strength. The value of quenching rate constants, k_q, and energy transfer rate constant, k_1, in encounter complex are changed by the cations as order of $Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+$.[1] The order of quenching rate constant obtained in this work is quite different from the order of salt effect which was obtained in the electron transfer reaction between anionic complexes ($Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$). [2]

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A25

Cleaning of Photoresist and Etch Residue from Low-k Dielectrics using Supercritical CO_2

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The traditional ash and wet cleaning technologies are facing challenges as the industry moves towards porous low-k material with higher aspect ratios and dual damascene Cu technology. The traditionally oxygen based ash technology will damage porous (and even dense) carbon containing dielectric materials and the high surface tension of liquid based wet clean solvents will not be able to reach into the high aspect ratio vias as the critical dimensions are reduced to less than 0.10 μm. Wet clean solutions potentially cannot be removed from the porous material, or leave residue behind. The use of $SCCO_2$ as a cleaning solvent for removing photoresist and etch residue from semiconductor wafers is a novel approach to cleaning porous low-k dielectrics. The process can combine both the ash and wet clean into one step and also eliminates the need for an additional drying step. By adding only small amounts (less than 30 ml per wafer) of co-solvent the process also reduces the materials cost for cleaning, while providing an environmentally clean process. The $SCCO_2$ process is developed on small (1 x 1.5 cm) wafer pieces mounted in a high pressure chamber. The chamber is heated and filled with liquid carbon dioxide and then pressurized to the desired pressure. A co-solvent mixture is injected and the cleaning takes place. It is also possible to perform several cleaning/rinsing steps after each other, with each step typically taking less than two minutes. The wafer pieces are examined by optical microscope and SEM. It will be shown that the $SCCO_2$ process can be successfully applied to a variety of process technologies ranging from front end applications, such as removing photoresist and residue from ion implant wafers, to dual damascene structures with Cu and porous low-k dielectrics. We will also show how the process can be used to repair low-k dielectrics damaged by an ash process. This is done by restoring not only the hydrophilic surface but also the bulk material and removing trapped moisture by extraction into the supercritical fluid. It is clear that the $SCCO_2$ process can replace both the traditional ash and wet clean technologies. Besides being compatible with the newest materials and technologies it will also dramatically reduce the amounts of solvents and water used. The process is a modular approach: it can be used as a stand alone application with up to eight modules on a central handler, or it can be combined with an etch tool, scrubber or metal deposition tool. This will allow both the footprint and cost of equipment in the fabs to be significantly reduced.

B1

A Microscopic Simulation of the Viscous Flow of Colloids

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We present the results of a fully microscopic simulation of the viscous flow of a colloidal suspension. Both the particles of the dispersed phase and those of the suspension medium were treated explicitly by representing the system as a mixture of large and small particles interacting via a short ranged potential energy function. The shear flow of this system was simulated by use of the Non-equilibrium Molecular Dynamics (NEMD) method using the SSLOD equations of motion using Lees-Edwards periodic boundary conditions with a Gaussian thermostat to remove the heat generated. The systems investigated were approximately neutrally buoyant suspensions with a variety of suspended particle to suspension particle size ratios and suspended particle volume fractions, ϕ. The zero shear rate viscosity coefficient, η_0 was found to be well described by the Einstein relation up to $\phi \approx 5\%$ whereas the Batchelor relation was found to be accurate up to $\phi \approx 13\%$. Also η_0 is shown to depend only on ϕ over the whole range of volume fractions studied here in contrast to our previous work on particles which different in mass but not in size. Shear thinning is observed in all these suspensions at high shear rate and a decomposition of the shear viscosity into its various components is given in order to interpret the mechanism of this shear thickening.

B2

Phosphate ester hydrolysis promoted by novel di- and trinuclear Zn(II) complexes with macrocyclic ligands

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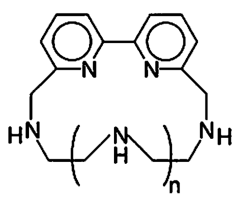
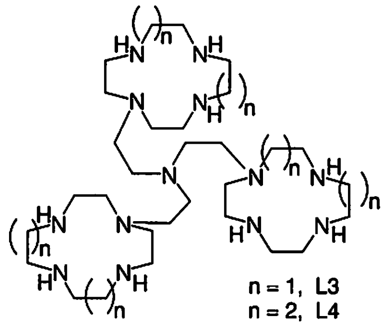
Macrocyclic ligands with a large number of donor atoms and cavities of appropriate shape and dimension may be able to hold two or more Zn(II) ions in close proximity, mimicking the multinuclear metal arrays at the active sites of several hydrolytic enzymes.



n = 3, L1
n = 4, L2



n = 1, L3
n = 2, L4

A potentiometric study on Zn(II) binding by ligands L1-L4 reveals that L1 and L2 form stable dinuclear Zn(II) complexes in aqueous solution, while L3 and L4 can also give trinuclear Zn(II) species.[1] The coordination environment of the metals is not saturated by the ligand donors, and, therefore, these complexes may behave as receptors for exogenous species. At the same time, facile deprotonation of coordinated water molecules occurs at neutral or slightly alkaline pHs to give Zn-OH functions. Actually, these complexes are able to promote the hydrolysis of bis-*p*-nitrophenyl phosphate (BNPP), through a mechanism involving a bridging coordination of the phosphate ester to two Zn(II) ions and simultaneous nucleophilic attack of a Zn-OH function to phosphorous. The different activity of the complexes in BNPP hydrolysis is discussed in terms of number of coordinated Zn(II) ions and coordination sphere of the metals.

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1) For ligand synthesis see: C. Bazzicalupi, A. Bencini, E. Berni et al. *J. Org. Chem.* 2002, 67, 9107 and *Dalton Trans.*, 2003, 793.

B3

Monitoring the reactions of polymers by MALDI-TOF Mass Spectrometry

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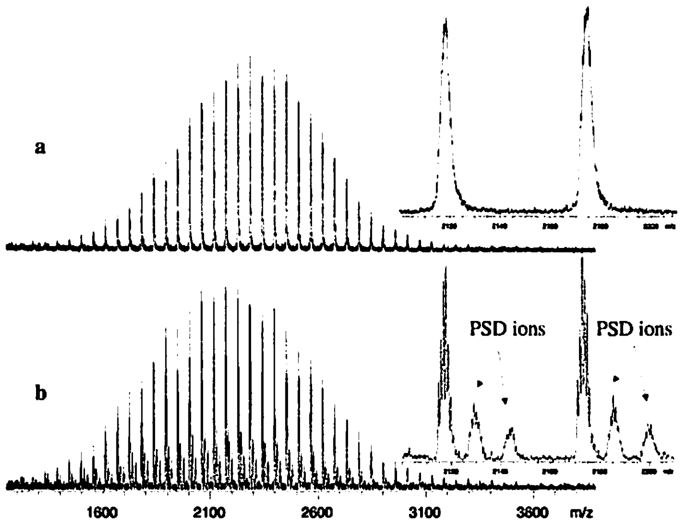
MALDI-TOF MS characterizations of different telechelic polyisobutylenes such as dihydroxy, bis(imidazole-1-carboxylate) and diamino functionalized PIBs will be presented. The synthesis of dihydroxy PIBs were achieved via epoxidation of α,ω-di(isobutenyl)polyisobutylene. The epoxidation was carried out at room temperature with dimethyldioxyrane (DMD), which proved to be a very effective reagent for the epoxidation without formation of side products. A very good agreement was found for the conversion determined by ^{1}H-NMR and MALDI MS. The kinetics of the reaction of α,ω-di(isobutenyl)polyisobutylene with DMD will also be presented. The epoxy end-groups were converted quantitatively to aldehyde termini using zinc bromide catalyst, then the aldehyde groups were reduced with $LiAlH_4$ into primary hydroxyl functions to obtain α,ω-di(2-methyl-3-hydroxylpropyl)polyisobutylene. The bis(imidazole-1-carboxylate) functionalized PIBs were produced from their corresponding dihydroxy derivatives. The dioamino terminated PIBs were obtained from the bis(imidazole-1-carboxylate) endfunctonalized polyisobutylenes. The MALDI-TOF MS spectrum of the bis(imidazole-1-carboxylate) telechelic polyisobutylene recorded in the linear (a) and in the reflectron (b) mode is shown below.



C1

INTERACTIONS OF URIC ACID – CONSEQUENCES FOR URIC ACID UROLITHIASIS

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The interactions of uric acid with some metabolites found in urine could have a significant effect on the solubility of uric acid in urine.

In the in vitro experiments, solubility of solid uric acid in saline solutions with ionic strength 0.15 (NaCl) was determined at 37 °C in a percolation cell [1] without or with the presence of several metabolites found in urine. Urea [2], glucosamine [3], and hippuric acid were studied more thoroughly changing their concentrations and initial pH of solutions. During kinetic measurements which lasted up to 24 h, pH in the solutions was monitored and at different time intervals the samples were taken for UV spectra and uric acid concentration determinations. The most peculiar behaviour showed uric acid in the solutions of urea, but some kind of interactions were also recorded in solutions with glucosamine, hippuric acid, formaldehyde [4] and glyoxalic acid. Computer modelling was used to characterize the uric acid interactions with urea, glucosamine, and hippuric acid.

The authors discuss their results in the view of uric acid urolithiasis as a protecting effect of some metabolites on formation of uric acid stones through increased solubility of uric acid.

Acknowledment

A partial financial support by IG4/13/2003 is appreciated.

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C2

Novel Approaches to the Structure of Functional Solvents and Elementarorganic Compounds with Saturated Hydrocarbon Ligands and their Solvates in Binary Systems

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Hydrogen bond gives prominence in particular at examination of associated interaction in liquid solvents and functional solvents (CH_3OH, C_2H_5OH, MF – methylformamide, DMF – N,N-dimethylformamide), but the specific intermolecular interactions in liquid saturated hydrocarbons of different classes and alkyl compounds of main group elements are not discussed. The thermodynamic properties are frequently used as the only origin for determination or evaluation of the intermolecular interaction energy in liquid compounds.

Illustrating this state by small number of examples, we pay attention to the fact that compounds with hydrogen bonds in liquid state differed essentially in evaporation enthalpies have close and even reduced enthalpy values in comparison with those for compounds, to which non-specific intermolecular interactions are ascribed.

	H_2O	C_2H_5OH	C_5H_{10}	$Zn(CH_3)_2$	$Al(CH_3)_3$
$\Delta_{vap.}H^\circ, kJ \cdot mol^{-1}$	37.43	43.31	25.77	30.40	41.30

The theory of associated liquids must solve the problem of principle disposition – to substantiate the structure and type of intermolecular interaction. This problem is very complicated, but its solution, in case of saturated organic compounds, functional solvents, compounds of non-transition elements with saturated hydrocarbon ligands, allows finding out the liquid state structure, nature of solvation process and determining energies of specific intermolecular interaction on the base of thermodynamic properties of one and two component liquids.

It is achieved on the base of the following regulations:

- ✓ substantiated refusal from sp^3-hybridization in CH_4 and molecules of elementorganic compounds with alkyl ligand;
- ✓ additional orbital dative type interaction in electron structure of main group element compounds with saturated hydrocarbon ligands and their coordination derivatives;
- ✓ pentacoordinated carbon atom in specific intermolecular interactions;
- ✓ employment of all bond vacancies in structure of molecules;
- ✓ enthalpy and entropy of evaporation are interconnected with number and energy of specific intermolecular interactions.

Besides, examinations of structures and specific intermolecular interactions in binary solution are based upon the Krestov's idea about predominant influence of component structure with some field choice.

The results of quantum chemical calculations of $Al(CH_3)_3$ structure are the base for refusal from sp^3-hybridization, which are used for conception development of dative bonding between carbon atom of alkyl ligand and central atom “A” of comlex AR_n. It is also established that:

- ✓ valent $2s^2$(C)-electron pair remains essentially localized on carbon atom even in CH_4 molecule and only two of four valent electrons of atom “C” situated on its three valent AO $2p_x$, $2p_y$, $2p_z$ take part effectively in hypervalent bonding with all of four hydrogen atoms;
- ✓ carbon atom of bridge CH_3-group (in particular $Al_2(CH_3)_6$) forms the fifth coordination with second atom “A” by dative mechanism using own valent electron pair and vacant orbital of central atom “A”. This principle correlates with the results of X-ray investigations of alkyl compound structures.

The possibilities of structural approach to thermodynamic analysis of solutions of binary alkyl systems, choosing distinctive solvates structures for each system and determination of energy of intermolecular interactions with participation of pentacoordinated carbon atom are discussed.

In the report we discuss a different types of specific intermolecular interactions with participation of pentacoordinated carbon atom of functional solvents (FA, NMF, DMF, DMSO) and calculated energies of hydrogen bonds in formamide (16.16 $kJ \cdot mol^{-1}$), and N,N-dimethylformamide (23.75 $kJ \cdot mol^{-1}$).

C3

Solution chemistry of dialkyltin(IV) - peptide interaction: equilibrium and structure

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Equilibrium and solution structural studies on the interactions of the highly toxic organotin(IV) cations with potential binders of biological fluids and tissues, or their low molecular weight mimics, may furnish essential details about (i) the solution state organotin(IV) compounds (ii) their possible transformations in the organism, (iii) their bio-availability and (iv) their interference into different physiological processes. Here, we report equilibrium and solution structural investigations on the complex formation of dimethyltin(IV) cation with a series of peptides and peptide-like compounds, by varying the side-chain and terminal donor groups [1-5]. Except of those, containing no terminal carboxylate group (*e.g.* glycyl-histamine [2]), in all cases $\{X,N^-,COO^-\}$ coordinated complexes ($X = NH_2$, $R\text{-}O^-$, $Ph\text{-}O^-$, S^-) have been found to be dominant in the neutral pH range. Thus, our results provided the first example, that alkyltin(IV) cations are able to promote the deprotonation of the peptide-nitrogen in aqueous solutions, at unexpectedly low pH. For the ligand with $X = NH_2$, $R\text{-}O^-$ or $Ph\text{-}O^-$, the amide deprotonation is promoted by the terminal carboxylate as anchoring group. The "N-terminal" thiol group induces fundamental changes: the primary binding site, and thus the anchoring group for the amide nitrogen deprotonation is the thiolate group [5]. The slow ligand-exchange processes of the amide-coordinated species allowed their structural characterisation by NMR: they possess trigonal bipyramidal structure, with equatorial position of the two methyl groups, which is not altered by the side-chaine donor groups (imidazole [2] or carboxylate [3]).

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C4

Hydrolytic cleavage of ribonucleotide monophosphates and polyribonucleotides by homo- and heterodinuclear metal complexes of a cyclohexane-based polyamino polyalcohol ligand

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The cleavage of phosphoester bonds of biomolecules in the living organisms are catalysed and mediated by phophoesterase enzymes that contain, in many cases, two or three metal ions in their active sites. The modelling of these centers by dinuclear (or trinuclear) metal complexes of low molecular weight ligands has been in the focus of bioinorganic-bioorganic research.

Aiming the development of functional phosphodiesterase models we investigated the activity of homo- and heterodinuclear copper(II) and zinc(II) complexes of 1,3,5-trideoxi-1,3,5-tris(dimethylamino)-*cis*-inozitol (tdci) on the hydrolytic cleavage of different mono- and diribonucleotide monophosphates and polyribonucleotides. The dinuclear copper(II) complexes of the ligand ($1.1 \cdot 10^{-3}$ M) induced 5-25000 fold rate enhancement on the hydrolysis of nucleoside-2',3'-cyclic-monophosphates whilst remarkable base and regioselectivity was also observed. Even higher rate enhancement was found in the solutions containing copper(II) and zinc(II) ions and tdci in equimolar ratio. In contrast with the homodinuclear species the ternary system efficiently promoted the cleavage of several dinucleotides (ApA, UpU, UpA, ApU) that suggests that a certain step of the mechanism (very likely the departure of the leaving group) is better catalysed by the heterodinuclear complexes. At 35 °C the half-life time of ApA decreased form *ca.* 4 years to 12.5 hours. Rate acceleration for the hydrolysis of polyribonucleotides amongst mild conditions was also observed in the ternary system.

This research has been supported by a Marie Curie Fellowship of the European Community program „Improving the Human Research Potential and the Socio-Economic Knowledge Base", contract number „HPMF-CT-2002-01860".

C5

Bis-(3-Hydroxy-4-pyridinonate) Derivatives and Metal complex Formation Equilibria

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In recent years considerable effort has been directed towards the development 3-hydroxy-4-pyridinones (3,4-HP) as metal chelating agents for medicinal applications. In fact, due to their high affinity for specific metal ions, they can be potentially used either as decorporation agents for certain metal ions (e.g. Fe and Al can accumulate in man and be responsible for serious diseases) or for chemotherapy or diagnosis, when complexed with radio-metals (e.g. ^{67,68}Ga, ^{111}I and ^{67}Cu).

As part of an ongoing project, we have explored the effect of the polydenticity of 3,4-HP's and the presence of extra functional groups, to account for improving the chelating affinity and the biological interaction, respectively. Accordingly three bis-hydroxypyridinone derivatives were designed. They have two of those binding unities coupled to two carboxyl groups of three different backbones, which differ in topology and the number/type of extra-functional groups.

Herein, we present and discuss the results of a set of equilibrium studies, performed in aqueous solution, for the characterization of these three compounds, namely in terms of their acid-base and lipo-hydrophilic properties, the evaluation of their binding affinity towards a set of M^{2+} (M = Cu, Ni, Zn), and M^{3+} (M = Fe, Al, Ga) ions and the estimation of the coordination modes. These studies are based on potentiometric and spectroscopic (UV-Vis, NMR and EPR) measurements. The discussion of the results is based on comparison of the different frameworks and extra-functional groups, on reported data for mono-derivatives.

Acknowledgement: We thank to the Portuguese *FCT* (project POCTI/35344/00), the Hungarian-Portuguese Intergovern. program and the COST D21/001 program for financial support.

(1) Santos, M.A., *Coord. Chem. Rev.* **2002**, *228*, 187.

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C6

Enhanced conformational changes of DNA in the presence of Mercury(II), Cadmium(II) and Lead(II) porphyrins in aqueous solution

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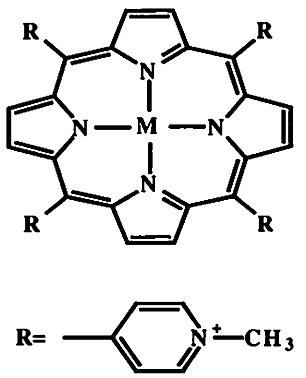
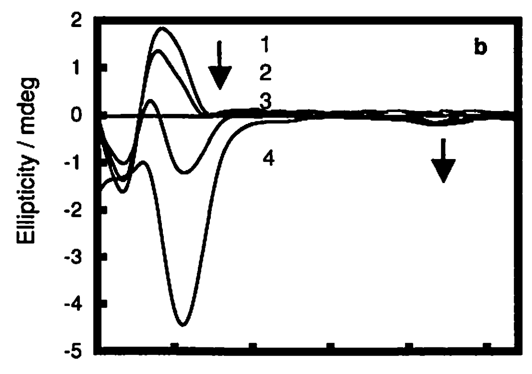
The interactions of the metalloporphyrins of tetrakis (1-methylpyridinium-4yl)porphyrin ($[M(TMPyP)]^{4+}$ where M=Hg(II), Cd(II) and Pb(II)) with pBluescript II plasmid DNA have been studied by the measurements of circular dichroism (CD), UV-visible and fluorescence spectra at 0.1 M $NaNO_3$, pH 7.5 and 25°C. The CD spectra of the DNA changed quite significantly, with the conformational changes in the presence of the metalloporphyrins being much more enhanced compared to that of their free metal ion counterparts. The conformational changes of DNA upon binding to the Hg(II) porphyrin and Hg(II) were, however, different from those of the Cd(II) porphyrin, Pb(II) porphyrin, Pb(II), Cd(II) and $H_2(TMPyP)^{4+}$. In the concentration range of 0 - 2.30 x 10^{-5} M of DNA, the absorption spectra of $H_2(TMPyP)^{4+}$ showed substantial hypochromicity at 423 nm and a red shift of $\Delta\lambda$ = 16 nm in the presence of DNA whereas the Hg(II)-, Pb(II)- and Cd(II) porphyrins showed blue shifts of absorption maximum wavelengths of $\Delta\lambda = -17$ nm, $\Delta\lambda = -35$ nm and $\Delta\lambda = -4.5$ nm, respectively. Furthermore, the shifted absorption maximum wavelengths/nm of the porphyrins in excess amount of DNA were comparable; 438, 439, 440 and 440 for $H_2(TMPyP)^{4+}$, Hg(II)-, Pb(II)- and Cd(II) porphyrins respectively. The changes in absorption spectra for Hg(II)-, Pb(II)- and Cd(II) porphyrins revealed that these metalloporphyrins dissociated upon binding to DNA which was confirmed by CD as well as fluorescence spectra. The CD results, UV-visible and fluorescence data indicate that the metalloporphyrins interact differently with DNA based on their binding modes. And the enhanced changes in conformation of DNA in the presence of the metalloporphyrins are due to the synergistic effects of the simultaneous binding of the metal ions and free base porphyrin to DNA compared to their free metal ion counterparts:

$$[M(TMPyP)]^{4+} + DNA + 2H^{+} \rightleftharpoons [\, M(II)(DNA)H_2(TMPyP)^{4+} \,]$$



M$(TMPyP)^{4+}$



CD spectral changes of DNA with $Hg(TMPyP)^{4+}$.

C7

The first reported Ru(III) hydroxamate complexes – speciation studies, structures and comparison with Fe(III) - hydroxamates

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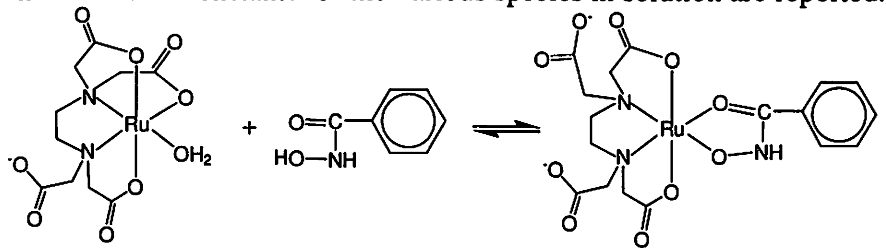
Hydroxamic acids are a family of weak organic acids of general formula, RC(O)NHOH and are found naturally in microbial siderophores where their chelating ability is utilised in the uptake of iron[1]. It was recently shown that hydroxamic acids are nitric oxide donors by their ability to react with ruthenium(III) complexes forming ruthenium(II) nitrosyls and physiologically to cause vascular relaxation of rat aorta by activation of the haem enzyme guanylate cyclase[2].

Reaction of $K[Ru^{III}(Hedta)Cl]\cdot 2H_2O$ with various phenylhydroxamic acids, R- PhaH, in aqueous solution affords the hydroxamate complexes $[Ru^{III}(H_2edta)(R\text{-}Pha)]\cdot xH_2O$, the crystal and molecular structure of one of which i.e. hydrated $[Ru^{III}(H_2edta)(2\text{-}OMe\text{-}Pha)]$ has been determined. In this complex, the carboxylato groups of the tetradentate H_2edta are *trans* to each other and the amino nitrogen and hydroxamate oxygen donor atoms are roughly coplanar. Addition of R-PhaH to the binary Ru^{III} – edta complex in aqueous solution resulted in $[Ru(edta)R\text{-}Pha]^{2-}$ as the major species at pH 4-7. At higher pH the hydroxamate NH groups in these complexes undergo deprotonation to give the hydroximato complexes $[Ru^{III}(edta)R\text{-}PhaH_{-1}]^{3-}$ as the major species at pH 7-11. This deprotonation, which has been reported in only a few previous cases is accompanied by marked shifts to longer wavelengths in the ligand to metal charge transfer bands. At pH>10 hydrolysis is observed and give $[Ru^{III}(edta)(R\text{-}PhaH_{-1})OH]^{4-}$ in which an edta carboxylato group has been replaced by hydroxide ion. Formation constants for the various species in solution are reported.



The affinity of Pha for $[Ru(edta)H_2O]^-$ (hexacoordinated) is much greater than for $[Fe(edta)H_2O]^-$ (heptacoordinated) but this is undoubtedly due to differences in charge and coordination numbers of the immediate coordination environments rather than intrinsic affinity differences between Ru(III) and Fe(III) for hydroxamate ligands.

Acknowledgements: We thank the EU Fifth Framework Copernicus 2, COST and Enterprise Ireland for financial support.

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C8

Electrospray Ionization Mass Spectrometry in Studies on Aluminium(III)-Ligand Solution Equilibria

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The application of electrospray ionization mass spectrometry (ESI-MS) in the study of aluminium(III)-ligand solution equilibria was examined. The advantages and the possible limitations were reviewed.

As an example, ESI-MS was used to study the complex formation between Al(III) and the two ligands 4-hydroxy-3-pyridinecarboxylic acid and 3-hydroxy-4-pyridinecarboxylic acid. The results were compared with the speciation data obtained from potentiometric, UV-vis, and NMR measurements. A very good agreement was obtained for the number and for the stoichiometry of the main species in solution, while their relative concentrations were found to be significantly different. This suggests ES-MS to be a powerful qualitative technique for the study of any aluminium(III)-ligand systems, even for very complicated ones, but on the other hand the accuracy of ESI-MS quantitative data is still questionable.

C9

Interactions of Histone H2A Peptides with Cu(II) and Ni(II). Hydrolysis and Oxidative Properties of the Species Formed.

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The last years we have been intrigued by the coordination chemistry of peptides modeling the C-terminal of histone H2A with toxic metals.[1] The hexapeptides $AcTESHHKNH_2$, and $AcTESAHKNH_2$ which represent modifications of the 120-125 sequence of H2A were synthesized and their interactions with Cu(II) and Ni(II) ions were studied. Both of them interact strongly with the metal ions in a wide range of pH.

At physiological or higher pH hydrolysis of the hexapeptides occurs. The tetrapeptides $SHHK\text{-}NH_2$ and $SAHK\text{-}NH_2$ produced, were synthesized by standard techniques and their interactions with Cu(II) and Ni(II) were also studied.

It was found that the dominant complex $CuH_{-1}L$ with hexapeptide -TESHHK- at pH 7.4 promotes efficiently the oxidation of dG with a transient formation of substantial amounts of 8-oxo-dG, in the presence of H_2O_2.

(1) Mylonas M., Krezel A., Plakatouras J., Hadjiliadis N., Bal W., *J. Chem. Soc., Dalton Trans.*, **2002**, 4296, and references cited therein.

C10

Solution Studies of 3-Hydroxy-4-Pyridinones with Biomedical Applications

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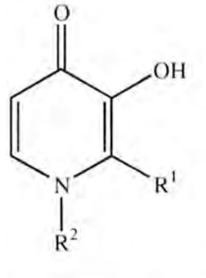
Pyridinone ligands are particularly attractive for pharmaceutical purposes because their structure allows tailoring of the hydrophilic/lipophilic balance (HLB), making them enough water soluble for oral administration and enough lipophilic to cross membranes, without significantly changing its chelating properties as is known for M(III) ions.[1] The pharmaceutical importance of pyridinones has already been recognized, in iron and aluminium chelation therapy, in radiodiagnosis and radiotherapy and more recently its vanadium(IV) complexes showed insulin-mimetic behaviour.[1,2]

In this work we report the interaction of N-alkyl-3-hydroxy-4-pyridinones with Co(II), Ni(II) and Cu(II) metal ions. Characterization of the species formed in aqueous solution for variable pH and M:L ratio is achieved by spectroscopic and potentiometric methods. The chelating affinity of the ligands towards Cu(II), Ni(II) and Co(II) is assessed by the values of stability constants and shows no significant variation with ligand lipophilicity.



$R^1 = CH_3, C_2H_5$ and $R^2 = H, CH_3, C_2H_5$

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C11

Simple blood tests of potentially insulin mimetic peroxovanadates

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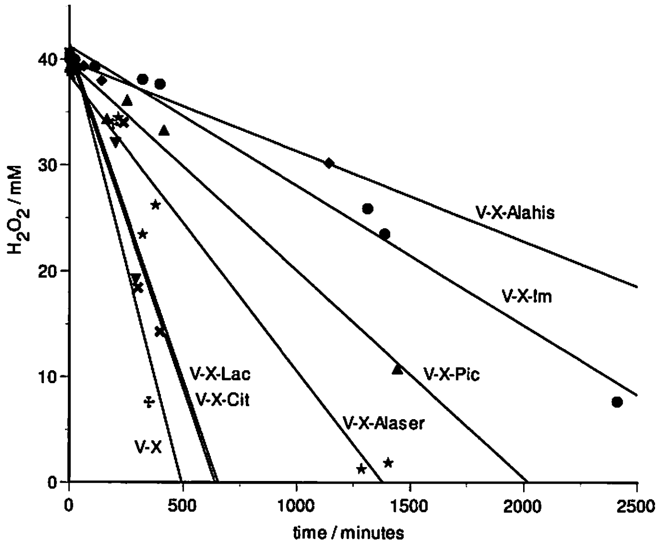
Vanadium is known for its insulin mimetic effect, which is synergistically enhanced by the addition of hydrogen peroxide, owing to the formation of peroxovanadates. Hence, the nature of these compounds became the subject of diverse studies in chemistry and medicine.



Simple tests were carried out to determine the stability of different peroxovanadate complexes against human catalase, the enzyme responsible for the decomposition of hydrogen peroxide in human blood. The purpose of the experiments was to investigate if catalase was able to recognize the peroxo ligand bound to vanadium as its substrate. In other words: could the introduced peroxovanadate complexes reach their target or would they decompose, making the nature of the original compound irrelevant with respect to their actual insulin enhancing effect? Solutions were prepared at pH = 7.4 in 150 mM Na(Cl) medium to represent both the pH and ionic strength of human blood. A total vanadium concentration of 20 mM was applied with a two fold excess of both hydrogen peroxide and one of the following ligands: picolinic acid (Pic), imidazole (Im), L-α-alanyl-L-histidine (Alahis), L-α-alanyl-L-serine (Alaser), citric acid (Cit) and lactic acid (Lac). Inorganic peroxovanadates were also included for comparison. After the addition of a few drops of freshly taken human blood, ^{51}V NMR spectra were recorded at certain time intervals to monitor the changes and to follow the loss of peroxide over time.

Results shown that the nature of the organic ligand plays an important role in the fate of peroxovanadate complexes in blood. Their effect can be predicted to some extent from speciation studies done under the same experimental conditions.

C12

Synthesis, proton and copper(II) complexes of a novel polyhistidine type ligand

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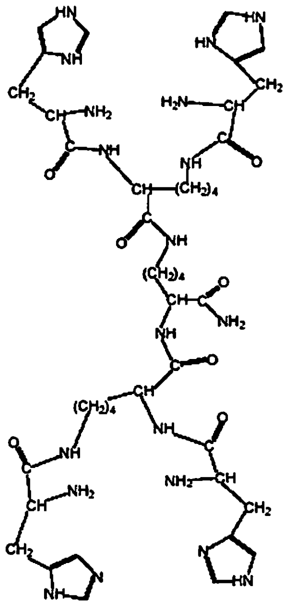

Histidines play an essential role in binding of biological metal ions, either in small or macromolecular chelating molecules, e.g. in metalloenzymes. Therefore the low molecular weight polyhistidine type ligands are of potential importance for use as model substances.

A novel branched oligopeptide type ligand (as shown in figure) was prepared by solid phase peptide synthesis. The ligand excerts eight primary protonation sites. As the pH potentiometric titrations revealed, the pK values for the deprotonation processes of these donor groups are close to each other indicating no or weak interaction among them. In addition to ammine and imidazole nitrogens, in the presence of copper(II)ions the amide nitrogens may loose protons, as well. Combined potentiometric, spectrophotometric and CD spectroscopic methods were utilized to investigate the speciation and the structure of the copper(II)complexes formed in aqueous solution.

The possible catalytic property of the complexes was also checked in the DNA cleavage assays.

This work has received support through SAPSTCLG97697 NATO Collaborative Linkage Grant and from the Hungarian Science Foundation (OTKA T43232).

C13

Acid-base chemistry of folic acid, methotrexate and related bioligands

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Folic acid (pteroylglutamic acid, B_{10} vitamine) and its reduction products play an important role in cellular DNA and protein synthesis as biological methylation agents and carrier of C_1 fragments. Folate antagonists, such as methotrexate, are antitumor drugs which block the key enzyme of folate metabolism, dihydrofolate reductase.

Folic acid and methotrexate contain several moieties which may undergo acid-base reactions in body fluids of various pH and permittivity. Protonation constants are widely used thermodynamic parameters in structure-activity relationships as well as to interpret enzyme binding and transport characteristics of bioligands. However, reliable basicity data are not readily available in the literature for these pteridine derivatives, mainly because of their poor water solubility at pH < 5.

In our study, several experimental methods have been applied to determine all protonation constants of folate, N^{10}-methyl-folate, 4-amino-folate, methotrexate and their „building blocks": pteroic acid, DAMPA and *N*-(4-aminobenzoyl)-glutamic acid. To overcome the solubility problem, potentiometric titrations have been carried out in various DMSO/water solvent mixtures and the protonation constants for the pure aqueous state were obtained by extrapolation. To verify the results, UV spectrophotometric and capillary electrophoretic titrations have also been performed at 10^{-4}-10^{-5} M concentrations in aqueous solutions.

① PRL 90, 75502 (2003).
K. Modig et al
1H NMR

② Science 278, 658 (1997)
fs Mid-IR

D1 MSPOM

New perspectives concerning water structure

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Abstract:

The establishment of a detailed structural picture for the structure of pure water or of aqueous solutions is a scientific challenge of utmost importance in chemistry, biology or physics. Following the recent advances in the reproducible synthesis of nanoporous architectures in the past few years, it is now possible to study through X-ray diffraction techniques aggregates of water molecules of varying sizes (from 4 to 100) and shapes. The currently state of knowledge in this field will be reviewed and discussed in terms of H-bond geometry (H-O…O bond angles distributions) and H-bond strength (energetic partition functions) based on the available experimental data. This provides for the first time a very clear picture of the structural response of H-bond patterns involving water molecules to a structural constraint (geometry of the encapsulating container) or to a chemical perturbation (presence of various anions and/or cations). With these new structural data in hands, we will try to throw some new light on some quite old problems concerning water structure (low-density versus high-density water, structure-forming versus structurebreaking behavior, nature of the hydrophobic interactions,…).

D2 MSPOM

Manipulating Polyoxometalates ?

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The bewildering and seemingly never-ending range of compositions and structures exhibited by the polyoxoanions of vanadium, molybdenum, and tungsten presents a challenge for rational understanding and control of this field. Is it possible for a chemist to design and synthesize a polyoxometalate with desired structure and properties, or is Nature manipulating (and tantalizing) us? The answer is of course a bit of both. Some progress towards synthetic design has been achieved by the use of so-called lacunary polyoxoanions as components of larger assemblies or as precursors of derivatized and functionalized polyoxometalates. New and recent work with lanthanide and actinide heteroatoms, stimulated by the use of polyoxometalates in nuclear waste treatment, and the use of trans-metallation processes with organotin groups will be discussed.

D3 MSPOM

Quantitative NMR Spectroscopy – An excellent tool

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One part of our research deals with inorganic polyoxometallates, so-called iso- and heteropolyanions, which have found many applications in catalysis, analysis, biochemistry, medicine etc. The other part comprises the complexation of vanadium to organic ligands that are significant from a biological point of view. Our goal is to determine speciation, dynamics and structures of complexes formed in aqueous systems. We have found that a combination of potentiometry and different NMR-spectroscopy techniques is a very powerful tool, making it possible to fulfil the goals. To establish the speciation, we use the computer program LAKE [1], which is designed to simultaneously treat multimethod data.

Recently, we have focused on peroxomolybdate and peroxovanadate systems. Peroxomolyb-dates have *e.g.* found applications in the bleaching process for kraft pulp (selective delignification). Peroxovanadates have received wide attention mainly due to their insulin-mimetic behaviour.

Our studies of the peroxomolybdate [2,3] and peroxomolybdophosphate [4] systems have been performed in 0.300 M $Na_2(SO_4)$ medium, since Na^+ and SO_4^{2-} are the most common ions present in the bleach processes. The peroxovanadate systems [5] have been studied in 0.150 M Na(Cl) to represent the conditions in human blood.

The strength of using quantitative NMR data for establishing the speciation will be exemplified from these systems. Some structural and dynamic results obtained from NMR measurements will also be addressed.

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[3] F. Taube, I. Andersson, I. Tóth, A. Bodor, O. Howarth, L. Pettersson. *J. Chem. Soc., Dalton Trans.* (2002) 4451-4456.
[4] F. Taube, I. Andersson, S. Angus-Dunne, A. Bodor, I. Tóth, L. Pettersson. *Dalton Trans.* (2003) In Press.
[5] L. Pettersson, I. Andersson, A. Gorzsás. *Coord. Chem. Rev.* 237 (2003) 77-87.

D4 MSPOM

Recent Progress in Peroxopolyoxometallates

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The basic chemistry of peroxopolyoxometallates (PPOMs) is still underdeveloped mainly due to difficulty in controlling peroxoide contents, complexity of the system and instability of the complex formed, while their use in *e.g.* oxidation reactions, pulp bleaching and metal oxide precursors is well-known. The author has been working with both speciation works in solutions and synthetic and structural chemistry of PPOMs. Here will be discussed structural features of the PPOMs obtained recently at our laboratory, and their relationship to the species found in solutions.

[Peroxopolyoxomolybdate - dimolybdate as a building unit]

The authors found novel peroxoisopolymolybdates such as $[Mo_2O_2(O_2)_4(OH)_2(OH_2)_2]^{2-}$, three isomers of $[Mo_4O_6(O_2)_8]^{4-}$ and a spiral polymer of $[Mo_2O_3(O_2)_4(OH_2)]^{2-}$ recently. All these anions have well-known $[Mo_2O_3(O_2)_4(OH_2)_2]^{2-}$, formed in the solution in wide range of conditions, as a building unit. This dimer acts as a building unit even in known trimeric and decameric peroxomolybdates, indicating a vast ability of this unit to construct a larger unit. An ^{17}O-NMR study is ongoing to elucidate the behaviour of the dimeric unit in solution.

[Peroxohetero- and isopolytungstate - tritungstate as a building unit]

There are some peroxoheteropolytungstates, *e.g.* $[HS_2W_3O_{14}(O_2)_3]^{3-}$ and $[H_2S_2W_6O_{23}(O_2)_4]^{4-}$, having a W3 moiety as a building unit. Several novel peroxohetero- and isopolytungstates have been obtained by the authors recently, and all of which have the W3 moiety as a building unit. This fact indicates the great ability of the W3 moiety. However, this unit has not been identified in solutions, either by ^{17}O-NMR or by ESI-MS. An ^{17}O-NMR study is ongoing to clarify the relationship between obtained and proposed structures of the peroxohetero- and isopolytungstates.

D5 MSPOM

Rational design of crystal tectonics driven by in-situ NMR

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Crystallogenesis of hydrothermally grown crystals has been a challenge for years due to the difficulty of investigation of solution species. Furthering the mechanism of condensation was thought to be inaccessible for a long time. Many attempts involving zeolite synthesis have been unsuccessful.

Since few years we have developed the tools for in-situ observation of the on-going synthesis inside specially designed "NMR hydrothermal tubes".

The syntheses can therefore be completely followed from the mixture of reactants to the crystal growth.

Several studies concerning nanoporous materials as AlPO4-CJ2, ULM-3 and ULM-4, SAPO-34, titanium fluorophosphate –TiFP-, MIL-74 as well as aluminium polycations Al13, Al30, Al32 will be used to exemplify the experimental strategies allowing to establish the mechanisms of crystal formation. The critical step to understanding the crystal tectonics is the nucleation stage at which the infinite network is formed.

The condensation steps leading to the infinite network, the transformation of the network into a crystal will be described and explained.

The relation between the crystal tectonics and the crystal topology is so strongly correlated that the crystallographic structure can be deduced from its crystallogenesis. This is the basis of crystal design and engineering.

Concerning polycations, their control is definitely more delicate than polyanions. The size reached by the polyanionic objects of Müller's group is well beyond what is currently achieved by the largest polycations known. However, we will show that the in-situ NMR observation tools help to better control the chemical parameters that allow to increase the size of the objects. Al13, Al30 and Al32 polycations produced under such internal control will outline the proposed strategy.

D6 MSPOM

Aggregation Behavior of Fullerene Surfactants in Aqueous Solution

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cburger@sunysb.edu.
[2]Dept. of Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan.

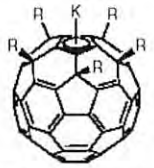

Figure 1: Chemical structure of $C_{60}R_5K$. R = (Ph, Me, $CH_2{=}CH{-}CH_2{-}$).

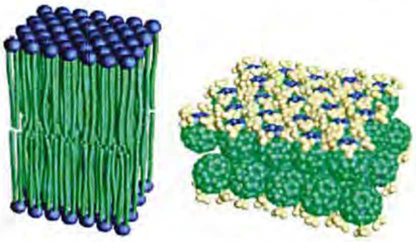
(a) Lipid bilayer. (b) Fullerene surf. bilayer.

Figure 2: Traditional lipid bilayer vs. fullerene surfactant bilayer.

While the extremely hydrophobic fullerene molecule C_{60} could be rendered water soluble in a straightforward way by attaching hydrophilic functional groups like amines or carboxylic acids, there exists a less obvious way to achieve this goal, consisting of the stabilization of the cyclopentadienide ring in its anion by suitable substituents, figure 1. This unique carbanion, a pure hydrocarbon compound with no hetero atoms, is not only soluble in water but has a peculiar surfactant functionality where the polar head group is given by the charged cyclopentadienide 5-ring and the hydrophobic part does not consist of a flexible hydrocarbon chain but of a compact and rigid hydrocarbon ball. Despite these significant architectural differences, fullerene surfactants are capable of arranging themselves into bilayer membranes comparable to those of traditional surfactants or lipids, figure 2. In aqueous solution, these fullerene surfactants tend to associate into large (30 – 100 nm) aggregates which can be studied by dynamic and static light scattering as well as by microscopic (TEM and AFM) techniques. In addition to the spherical bilayer vesicles, figure 3(a), observed previously[1] for R= Ph, the compound with R= Me shows concentration dependent transitions to more elaborate aggregate geometries like multi-shells, figure 3(b), and clusters of vesicles, figure 3(c).[2]


(a) Bilayer vesicle. (b) Multi-shell vesicle. (c) Cluster.

Figure 3: Fullerene surfactant vesicles geometries. Sectors are cut open to enhance visibility of the models.

Financial support by the U.S. Department of Energy (DEFG0286ER45237.016), the National Science Foundation (DMR-9984102), and the JapaneseMinistry of Education, Culture, Sports, Science and Technology are gratefully acknowledged.

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D7 MSPOM

Model Polyelectrolytes: Electrostatic Self-Assembly and Nanotemplating

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The synthetic design of nanostructures has recently come into focus due to the potential for new "smart" materials. To be able to take advantage of such nanostructures, it is necessary to create them in a controlled manner, understand formation mechanisms and properties. We here investigate structure formation based on polyelectrolytes.

Polyelectrolytes are widely found in nature and applications and show special effects like the increase of reduced viscosity upon dilution or the "extraodinary regime" with two diffusion processes. However this class of substances is far from being fundamentally understood, mainly due to a complex interplay of inter- and intramolecular interactions. Therefore, we study polyelectrolytes of fixed geometry as model system. Only intermolecular interaction plays a role and can be studied quantitatively. Polyelectrolyte microgels, small spherical hydrophilic polyelectrolytes allowed us to investigate the formation of ordered domains in solution quantitatively and conclude that the driving force of the effective attraction between the like-charged macroions is electrostatic in nature and due to the counterions.[1,2]

The interaction of polyelectrolytes and counterions is further used for the design of structures on the nanometer length scale. The self-assembly of charged dendrimers with gold ions in aqueous solution was used as precursor for the formation of dendrimer-templated inorganic nanocrystals of a well-defined size. Small angle x-ray scattering (SAXS), small-angle neutron scattering (SANS) and transmission electron microscopy (TEM) allow characterization of the hybrid particles. Semiconductor quantum dots and solid composite materials can be obtained via the same approach. Apart from yielding well-defined hybrid particles, dendrimers with a size of 1 to 15 nm represent a model system covering the range from a typical low molecular mass molecule to a typical polymer or colloid. Interestingly, the stabilizing mechanism changes from classical colloid stabilization for the lower generation dendrimers to polymer nanotemplating for higher generations. [3-5]

Further, we use "electrostatic self-assembly" of macroions and counterions to form supramolecular architectures. We use organic counterions of a certain geometry, both monovalent and multivalent ones, in order to direct the structure of the assembly. Goal is a fundamental understanding of the interaction forces influencing the self-assembly (electrostatic, hydrophobic, stacking of aromatic compounds as well as geometric factors).

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D8

Supramolecular assemblies in liquids: structure, thermodynamics, and macroscopic properties

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New approaches to describing supramolecular structure, molecular thermal motion, and the physicochemical properties of liquid mixtures on the basis of the generalized quasichemical models of the processes, occurring in matter during molecular thermal motion have been developed. Models of thermodynamic, dielectric, optical fluctuation and relaxation properties of liquid non-ideal systems determined by the molecular parameters of a different nature are constructed.

Methods for studying supramolecular ordering in liquids due to non-covalent intermolecular interactions such as the hydrogen bonds, and describing of structure and properties of aggregates, thermodynamics of their formation, and integral and differential parameters of aggregation have been developed. The methods presented allow to studying long range molecular correlations outside the nearest coordination shells, which are inaccessible to study other experimental techniques.

For the first time long range molecular correlations in liquids, self-organised by H-bonding were revealed. Structure, properties and thermodynamics of formation of supramolecular aggregates consisting of tens of molecules of nanosizes are investigated. The comparison with the computer simulation data is presented.

The macroscopic manifestations of supramolecular ordering in equilibrium and kinetic properties of liquid systems and phenomena, proceeding in them are discussed.

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D9

New Electronic Materials through Cooperative Self-Organization of Zintl Clusters and Surfactants

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This talk will focus on the formation of new electronic materials through inorganic/surfactant co-assembly. In this work, we use Zintl clusters, reduced main group clusters, as building blocks for new semiconducting materials. Using the examples of pure Ge and a variety of metal tin telluride alloys, we show that semiconductor/surfactant composites and periodic nanoporous semiconductors can be synthesized using the ideas of electrostatically driven solution phase self-organization. We first explore the self-organization process itself to understand how conditions such as charge density, inorganic oligomerization, and ionic strength control the structures of our nanoscale composites. We next examine the structure of these materials, characterizing their properties on both that atomic and nanometer length scales. Figure 1 shows an example of a low angle X-ray diffraction pattern of a germanium/surfactant composite produced by solution phases assembly of germanide cluster anions with cationic surfactants; the peaks index to a hexagonal honey-comb structure. Finally, we can examine the optical and electronic properties of these narrow band gap semiconductors and show how these properties can be tuned by changing size, surface structure, or chemical composition.

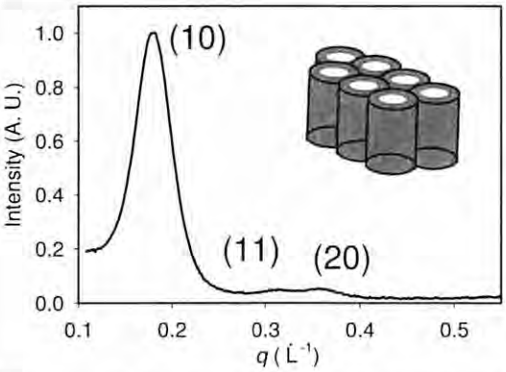

Figure 3 – Low angle X-ray scattering showing the hexagonal structure of the surfactant templated Ge. The inset shows the cluster building blocks that form the initial

D10

The mechanism of the Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene

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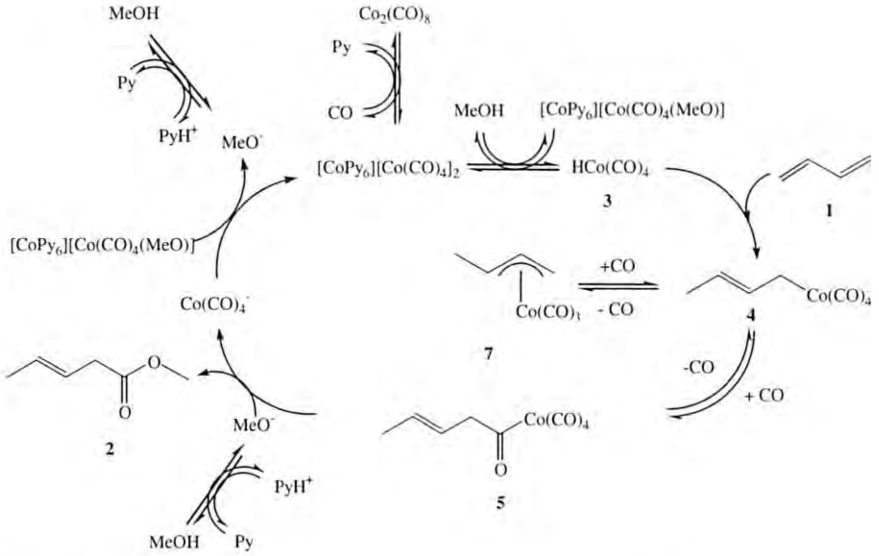
The hydromethoxycarbonylation of 1,3-butadiene (**1**) to methyl 3-pentenoate (**2**) could be the first step in the green production of adipic acid or ε-caprolactam, which are key intermediates in nylon manufacture. $Co_2(CO)_8$ in the presence of pyridine (Py) represents one of the few known catalyst systems which is suitable for this reaction. Although several different mechanisms have been proposed for this system, no intermediates have been isolated and characterized under reaction conditions. Our high-pressure IR and NMR study on the pyridine modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene led to the characterization of several key intermediates and the establishment of a detailed catalytic cycle:



Members **2**,**4**,**5**,**7** of the catalytic cycle were identified by high-pressure, multinuclear ^{1}H-, ^{13}C-, ^{59}Co-NMR measurements working in 10 mm sapphire tubes. At temperatures around 220 K corresponding cis-/trans- and syn-/anti- isomers were also detected.

E1

Hydration and Na^+Cl^- Pair Association in High-Temperature Aqueous Solutions along Sub- and Supercritical Isotherms.

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An extensive molecular-based study of ion-pair formation in near-critical dilute aqueous *NaCl* solutions is performed along three near- (super- and sub-) critical isotherms and from liquid-like to steam-like densities [1]. The study encompasses the determination of the ion-pair association constant via potential of mean force calculations. The main goal is to find answers to some relevant questions regarding the thermodynamic and corresponding microscopic behavior of the ion-pair formation at steam-like densities, where experimental data are either scarce or extremely difficult to obtain accurately. In particular, we address the density dependence of the 'mean hydration numbers' for the ion pair along a near-critical isotherm, the accuracy of the dielectrically screened potential model for ion-pair association, testing the adequacy of the intermolecular model to represent the actual ion-pair behavior in steam, and assessing the hypotheses invoked in current theoretical development on the modeling of ion association in steam-like solutions. Toward that end we make direct contact between simulation, theoretical developments and experiment to aid the interpretation of experimental data and their macroscopic modeling.

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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E2

Volumetric Studies of Binary and Ternary Aqueous Solutions Containing 2,2,2-Trifluoroethanol, Alcohols and Acetone at Temperature 298.15 K and Pressure 101 kPa.

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Aqueous solutions of trifluoroethanol have wide range of applications as cleaning agents, reacting media, refrigerants and fuels. They have been selected and subjected to various dynamic testing stability. Moreover, (trifluoroethanol+ alcohols, +glycol-ethers) solutions are proposed and selected as organic working thermal fluids for heat engines, absorption pumps and heat transformers. In bioengineering, trifluoroethanol and its water solutions are reported as stabilizers for peptide helices.

In this work, we report precise experimental data of volumetric properties of homogeneous binary and ternary liquid solutions containing 2,2,2-trifluoroethanol, methanol, ethanol, propanol, butanol, hexanol, heptanol, acetone and water at 298.15 K and 101 kPa.

The mixing thermodynamic properties of the ternary aqueous solutions and of pseudo-binary solutions are well fitted and predicted by various equations. The strong electronegative inductive effects of the fluorine atoms in trifluoroethanol make it a better proton donor than the alcohols. Water forms more hydrogen bonds than alcohols combing three-dimensional links. Upon mixing, (trifluoroethanol+water+alcohol) solutions show strong self and cross-associative behaviour. The Thermodynamic properties of theses systems will be further correlated using calorimetric and vapour-liquid equilibrium data.

E3

Structure of Supercritical Aqueous Alcohol Binary Mixtures

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Supercritical methanol-water binary mixtures have been measured at 0.2, 0.3, and 0.4 methanol mole fractions as a function of pressure by Raman spectroscopy to investigate the microscopic structure in terms of hydrogen bonding. Furthermore, small-angle neutron scattering (SANS) measurements have been made on supercritical aqueous binary mixtures of methanol and ethanol at 0.3 and 0.2 alcohol mole fractions, respectively, as a function of temperature and pressure to determine the mesoscopic structure information, such as the density fluctuations and the correlation length.

The pressure and concentration dependent Raman spectra of the stretching OH bands of water and methanol have shown that the degree of hydrogen bonding at the reduced pressure of unity changes to a large extent between the 0.2 and 0.3 mole fractions. The SANS data were analyzed by using the Ornstein-Zernike equation to obtain the density fluctuations and the correlation length as a function of pressure and temperature. It has been found that the maxima of these parameter values lie on the extrapolated line from the liquid-vapor equilibrium one to the supercritical regime; the result suggests that a trace of phase transition between liquid and vapor is present even in the supercritical state. The density fluctuations decrease as aqueous ethanol mixture > aqueous methanol mixture, but the correlation lengths do vice versa. The present findings are discussed in connection with the solvent clusters and reactivity in aqueous alcohol binary mixtures under the supercritical conditions.

11:46 - 12:06

E4

Development of High-Pressure Magnetic Resonance Imaging for In-Situ Observation of Supercritical Fluid Solutions

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We have developed several kinds of high-pressure NMR cells for in-situ observation of supercritical fluid solutions.[1-3] In order to monitor ***macroscopic*** behaviors in a high-pressure cell directly, we newly present a multi-functional large-volume magnetic resonance imaging (MRI) cell, of which the schematic drawing is given in Figure 1. A sample solution is located in the cylindrical high-pressure cell and heated (or cooled) in three directions independently. The high-pressure cell is installed into a MRI probe and used for acquiring a 2D or 3D image. In the presentation, we will discuss the mixing process in two-component systems measured by MRI in the absence and presence of convection flow.

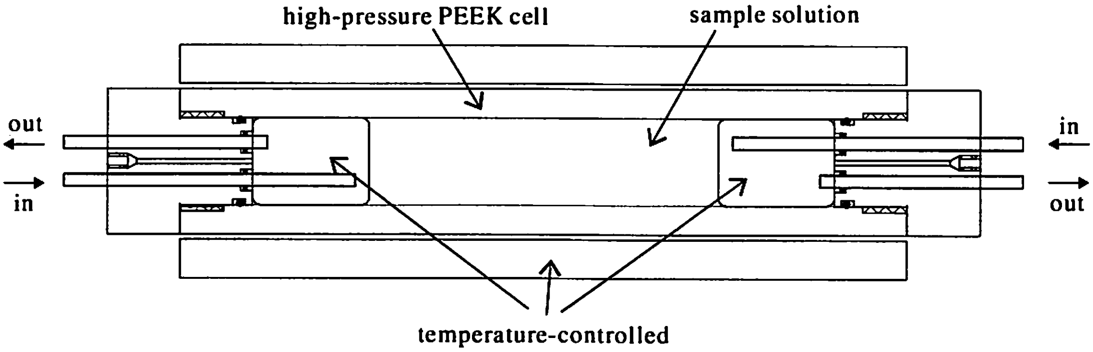

Figure 1. A schematic drawing of high-pressure MRI cell

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12:08-12:28

E5

Variation of hydrogen bond strength with solute concentration in glassy aqueous electrolyte solutions

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Although there have been many Raman studies of aqueous electrolyte solutions$^{1)}$, there have been only a few devoting to glassy aqueous solutions$^{2,3)}$. Raman spectroscopy is a powerful method for probing hydrogen bond strength in aqueous solutions. As glassy state represents the liquid structure at the lowest temperature, it is interesting to see the structural changes of glassy aqueous solutions with electrolyte concentration.

Here we have measured uncoupled Raman OD stretching spectra for a number of glassy aqueous electrolyte solutions to see how the hydrogen bond strength varies with electrolyte concentration. The uncoupled OD stretching Raman spectrum was decomposed into two components by the least square curve fitting method. The frequency of the high frequency component (ν_h) varies only a little with solute concentration while that of the low frequency component (ν_l) decreases rather linearly with decrease in salt concentration expressed by R (R = moles of water/moles of salt). It is evident that the high frequency component is mainly ascribed to the uncoupled OD stretching vibrations of the water molecules directly hydrogen bonded to anions. Perchlorate ion gives the highest ν_h value and fluoride ion gives the lowest ν_h value among the anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, acetate ion and ClO_4^-) investigated. On the other hand, every ν_l value decreases in frequency with decrease in salt concentration, heading for the value (2440 cm^{-1}) of amorphous ice. We will compare the values with those for the solutions at room temperature.

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12:30 -12:40

E6

Thermodynamic model of dilute NaCl(aq) solutions in the critical region of water

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Completely dissociated aqueous solutions of alkali halides are successfully modeled to about 500-600 K for instance by the ion-interaction equations[1]. At higher temperatures and concentrations the ions associate to neutral molecules or clusters, calling for some "effective chemical continuum" treatment such as that proposed by Anderko and Pitzer[2]. Neither approach is, however, suitable for the intermediate region of near-critical temperatures and low solution concentrations, where the ions are only partially associated and thermodynamic properties are subject to rapid changes. A Helmholtz free energy model coupled with chemical association was proposed recently[3] for these systems. Standard state part of the model applies the SOCW equation-of-state[4] and the excess part comes from the Mean Spherical Approximation. The model was used for simultaneous correlation of experimental apparent molar volumes, apparent molar heat capacities and heats of dilution of dilute NaCl(aq) solutions at temperatures from 573 K to 723 K and at concentrations where the solutions are partially associated. Conversion from MacMillan-Mayer to Lewis-Randall reference state was performed using the full expression given by Friedman[5]. Performance of the model for data description is good, suggesting its application for other associating electrolytes in a wide range of state conditions.

Acknowledgement: J.S. was supported by the Grant Agency of the Czech Republic, contract No. 203/02/0080 and by Research Plan MSM 254100303. The Department of Energy is acknowledged for support by grant DEFG01-89ER-14080.

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F1

Theoretical Studies of Ethanol-Water Soluitions at Various Concentrations

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Monte Carlo calculation results for pure ethanol and water-ethanol mixtures calculated in the isothermal and isobaric ensemble at T=300K are presented. The analysis of hydrogen bounding between ethanol molecule and water molecules at molar concentrations of ethanol was done. The results obtained for the average energy interactions as function of the mole fraction show an increase in water-water interaction energy when the interaction between water and organic liquid molecules decreases. Radial distribution functions for water-ethanol interaction show characteristics features of hydrogen-bonded liquids. Radial distribution functions for water-water interactions calculated in pure water and water-ethanol mixtures are compared.

F2

Molecular Hydrodynamics: from Kubo to Smoluchowski

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In colloidal solutions as well as in porous media filled by a solvent, the dynamics of solvent and solute particles can be described at different levels:

- Molecular level where transport coefficients are derived from Kubo relations.
- Solvent averaged level where the dynamical quantities are obtained from Brownian dynamics simulations and calculated by an appropriate adaptation of the linear-response theory.
- Hydrodynamic level where the dynamics of solvent and solute particles are evaluated by solving the Navier-Stokes equation by Smoluchowski scheme, which can be related to the Kubo formalism.

For charged colloids [1] and charged porous media, we present applications of the above analysis. Practical examples of the three methods are given for very different systems such as charged micelles and swelling clays [2-3].

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F3

Iterative determination of pair potentials from diffraction data

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The popularity of classical mechanical simulations demands pair-potentials for many new systems. The most detailed experimental information about the structure of liquids can be obtained by x-ray and neutron diffraction techniques. The 'inverse theorem' of statistical mechanics offers an opportunity to determine the pair-interactions solely from the diffraction data, but it does not say how to do it exactly. Besides the many approximate variants of the well-known integral equation theory there are methods using computer simulations.

A method is developed to obtain tabulated pair potentials or analytic pair-potentials for liquids from structure factors or scattered intensities. A step of the iterative process consists of two parts: a simulation with an assumed pair potential and the modification of the potential due the experimental data and different quantities calculated in the simulations. The choice of the structure factor as input function makes it possible to avoid the difficulties of the Fourier transformation from the inverse to the real space, to replace the solution of the linear equations with simple linear combination in the case of multi-component or molecular systems, and to use least-square fit for the modification of the pair-potential.

The method is tested for one- and two-component Lennard-Jones systems, Lennard-Jones parameters for liquid argon are determined from a diffraction experiment[1]. We determined effective pair potentials in a tabulated form for liquid mercury at 10 different densities to investigate the structural changes around its metal/nonmetal transition[2]. Determination of tabulated pair potentials for colloids is in progress.

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F4

Theoretical calculations of ion hydration with different water models

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We compare hydration structures and energies calculated from common models of water (SPCE model) and ions (Palinkas, Riede, Heinzinger), with the results using some new models of water. These new models are

(i) a 3-site model developed in a RISM/SCF combined quantum-mechanical and statistical approach [1] and its variations.

(ii) a simplified 2-site model of water developed on the basis of Collins' model with the help of integral equation and simulation methods.

Both models show the characteristic features of the open network structure of water and also comparable structures of solvation shells around alkali metal and halide ions.

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F5

STRUCTURAL DYNAMICS OF WATER AND ITS SPECTRA OF ORIENTATION POLARIZATION.

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The structure-kinetic model of water is suggested. It is connected with the reaction of partial dissociation of polymer network and the transition of water molecule from the state in tetrahedral H-bond net to state in H-bond chain (in the initial framework). The model is used for explanation and calculation of dielectric spectroscopy data in frequency range $0< \nu < 800$ cm^{-1}. The mechanism of elementary movements of molecules in liquid water is considered on the basis of this model, experimental (in the range 80-120 GHz) and literature (up to 800 cm^{-1}) dielectric, absorption data and semiphenomenological confined rotator (I)/ confined rotator (II) /..../ confined rotator (N) theoretical scheme. The spectra of complex dielectric permittivity and absorption in far IR, submillimeter and microwave region are described. The difference between ordinary and heavy water is explained in all frequency range. The high frequency boundary of debye relaxation zone is determined. The structural dynamics of water in aqueous nonelectrolyte solutions is considered on the basis of the suggested model. The peculiarities of hydrophobic hydration are established.

The model is supported by computer simulation results (Monte-Carlo method) The computer investigation of the water structure is carried out on the basis of system consisting of 512 particles of water (in case of SPC, SPC/E and ST-2 potentials, T = 298K). The spatial arrangement of particles on the distances of short-range order (up to 7-10A) is considered using new method of analysis of spatial relationships between water molecules in configurations of the some or different coordination numbers and local density.

This work is supported by Russian Foundation Basic Research Grant No 01-03-32041.

F6

MD Simulation of Crystal Growth of NaCl from its Supersaturated Aqueous Solution

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We have performed MD simulation of crystal growth of NaCl from its supersaturated aqueous solution. To our knowledge, this is the first successful trial of crystal growth from electrolyte solutions by MD simulation.

Model: In a basic cell, 4 layers of NaCl crystal consisting 4x64 ions were arranged as the "seeds". Above the crystal, 192 H_2O molecules and 40 (Na^++ Cl^-) ions were disposed, and then mixed well at 300 K, while the lower crystal was kept at 0 K. The ratio of H_2O/Na is about 360/40 at 300 K (experimental data). The crystal was arranged so that the interface was the (100) plane. In the x- and y-directions, periodical boundary conditions were imposed, while in either z-direction the system was open to a vacuum. The Na^++Cl^- ions on the bottom layer were kept unmoved during the whole runs so that the system were stable in the z-direction. After some runs for equilibration of the solution phase by using other pair potentials than used in the following crystallization process, temperature of either phase was set to 300 K, when it was tentatively regarded as t=0. As the pair potentials for Na^+-Na^-, Na^+-Cl^- and Cl^- -Cl^-, the Tosi-Fumi potentials were employed, and for the other 7 (inter-molecular) pairs, available potentials[1-4] were used. As the model of H_2O, the BJH (flexible) potentials were used. During the first 360 ps, the temperature was kept constant, and then, constant energy runs with an exception of 1st layer (0 K) and 2nd one (300 K) followed for about 2.1 ns.

Results: An increase of the coordination numbers of Cl^- in place of O about Na^+ was observed. A similar trend was found for the coordination of Na^+ in place of H^+ around Cl^-. Coordination of a Cl^- and dehydration of an H_2O around an Na^+ took place nearly at the same time. After about 1000 ps, crystal growth of NaCl attached to the seed crystal was detected on the 5th and 6th layers.

Conclusion: Under the model employed here, the crystal seemed to develop in the liquid phase at first, and then the cluster attached to the seed crystal, by which crystal grew.

It depends on the potentials employed whether the crystal grows or not at all. Crystallization of the present aqueous solution system did not follow the continuous growth mechanism which is valid for NaCl melt.

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F7

Reverse Monte Carlo modelling of the microscopic structure of aqueous electrolyte solutions

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The Reverse Monte Carlo (RMC) method of structural modelling [1] has been applied for studying the microscopic structure of various disordered system, including the disordered (liquid [2] and amorphous solid [3]) forms of water. In a nutshell, the RMC procedure uses experimental (mostly diffraction) data as input and provides sets of atomic coordinates ('configurations') that are consistent with these data within errors. These configurations can then be subjected to further analyses.

Although there have already been a few applications of RMC for the investigation of the structure of aqueous electrolyte solutions, these systems have mostly been avoided, probably for their complexity (too many - at least 4 types of atoms - components, difficulties with neutron diffraction for hydrogeneous samples, etc.). Here we would like to propose a possible way (something like a 'protocol') of approaching these important materials, based on the simultaneous RMC modelling of one X-ray and - at least - one neutron total structure factor (as contrasted to the modelling of the partial pair correlation functions).
Geometrical constraints, as applied during the study of pure water (see, e.g. [2,3]) have also been introduced, in order to include information from other (than diffraction) sources. Since the O-O, O-H and H-H partials in most cases dominate the measured total structure factors, it is suggested that studies should be focused on the change in terms of the water structure.

As a first example, results for aquaeos LiCl solutions as a function of the salt concentration will be presented.

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F8

A comparative molecular dynamics study of the hydration of lanthanide (III) cations using *ab initio* based flexible and polarizable model potentials

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The interest in lanthanide (III) (Ln^{3+}) complexes ranges from liquid-liquid extraction from aqueous solutions to their spectroscopic and magnetic properties. The paramagnetic properties of Ln^{3+} ions make their complexes suitable as contrast agents in magnetic resonance imaging (MRI) diagnostic techniques and as shift reagents in NMR analysis of electrolytes in biological tissues. The ability of the complex to enhance the image contrast is related to its relaxivity, i.e. the degree to which it increases the relaxation rate of water protons. Among other factors, relaxivity is affected by the chemical exchange between water molecules in the first solvation shell and the bulk solvent. Due to the high magnetic moment of the Ln^{3+} ions, the experimental investigation of Ln^{3+} complexes in solution cannot be easily performed. Instead a self-consistent theoretical approach must be used. This approach should account for the decrease of atomic and ionic radii along the Ln series, which is due to an incomplete screening of nuclear charge by the *4f* electrons plus relativistic effects. It should also account for the deformation and the polarization of the water molecules induced by the high charge of the cation. Here we present a molecular dynamics study of the hydration of Nd^{3+} and Yb^{3+} performed with the *ab initio* based flexible and polarizable MCDHO[1] model potential for water. The cations were modeled in a consistent manner by fitting the parameters to ion - water interaction energies computed at the MP2/aug-cc-pVDZ level with counterpoise correction, using quasi relativistic effective core potentials[2] for the ion and allowing the relaxation of the water molecules.

[*]On sabbatical leave from CCF-UNAM, Mexico, and supported by NWO (433.078, The Netherlands), by CONACyT (020194, Mexico) and by DGAPA-UNAM (Mexico).

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F9

The fluctuation on theorem for ideal mixtures

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Using a simple combinatorial model we show that the fluctuation theorem holds for the nonequilibrium transient process of mixing in ideal mixtures of two-component fluids. We show that the fluctuation theorem is very closely connected to the phenomenological formalism of reaction kinetics, in particular, to unimolecular reactions.

F10

Thermodynamic properties of ethane in the critical region

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Abstract:

The thermodynamic properties of fluids can be predicted using global equations of state. Among these thermodynamic properties, we consider the densities of the liquid and vapor phases of fluids. In this work, we present the application of the crossover model to the vapor-liquid rectilinear diameter of ethane We also present the comparison of the crossover model equation of state with the experimental data.

Keywords: Crossover model, fluids, rectilinear diameter, ethane.

G1

Complex Formation of Biodegradative Chelating Agents

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Various kinds of aminopolycarboxylates represented by EDTA have been developed and applied to analytical chemistry and industrial purposes. EDTA is one of the high production volume chemicals and discharged to environment. Since it does not undergo biodegradation in the wastewater treatment or natural system, it is suspected that the accumulation of such a chelating agent in surface water causes a significant environmental impact. Thus, the environmental exigency requires the development of biodegradative chelating agents.

It is expected that the aminopolycarboxylates become biodegradative by the substitution of the iminodiacetic acid (IDA) group by the aminomalonic (AM) or aminosuccinic acid (AS). According to this line, we have synthesized several chelating reagents and studied the complex formation with metal ions.

In the present paper, ethylenediamine-*N,N'*-dimalonic acid (EDDM) and its methyl derivatives were synthesized and the complex formation constants with alkaline earth metal ions were determined by pH titration and NMR-pH measurements. Protonation constants of (*N,N'*-dimetylethylendiamine-*N,N'*-dimalonic acid; DMEDDM) are larger than those of EDDM because of the increase in basicity of nitrogen atoms by the methyl substitution. The complex formation constants of AM or AS type ligans (e.g., EDDM) are generally much smaller than those of IDA type (e.g. EDTA) by a structural requirement. Nevertheless, the stability constants of DMEDDM are peculiarly large and comparable to those of EDTA. NMR measurements revealed that the ligand exchange reaction of DMEDDM complexes of alkaline earth metal ions is extraordinarily slow, although the ligand exchange of alkaline earth metal is generally very fast.

G2

Existence of two UV spectrometrically distinguishable forms of nitrate ion in dilute aqueous solutions

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Two well-defined isosbestic points (at 265 and 313 nm) were found in the UV absorption spectra of dilute (0.06 mol dm^{-3}) aqueous solutions of $NaNO_3$, KNO_3 and $(NMe_4)NO_3$, measured at 13 temperatures in the (10...70) °C range. This finding, together with the apparent cation-independence of the spectra (confirmed by several statistical tests) indicates the existence of a chemical equilibrium between two species differing in the structure of solvation shells: $\alpha\text{-}NO_3^-$ Φ $\beta\text{-}NO_3^-$. Assuming the constancy of standard conversion enthalpy, $\Delta_r H^o$, in the experimental temperature range, a simple nonlinear programming algorithm, maximizing the linearity of $\ln K^o$ *vs.* $1/T$ relationship, was devised in order to compute optimized estimates of $K^o(T)$, $\Delta_r H^o$ and $\Delta_r S^o$, as well as the individual spectra of $\alpha\text{-}NO_3^-$ and $\beta\text{-}NO_3^-$ species. The following results were obtained: K^o ranges from ≈0.08 (10 °C) to ≈0.25 (70 °C), $\Delta_r H^o = 15$ kJ mol^{-1}, $\Delta_r S^o = 31$ J K^{-1} mol^{-1}, $\lambda_{max}(\alpha\text{-}NO_3^-) = 301$ nm, $\varepsilon_{max}(\alpha\text{-}NO_3^-) = 7.8$ cm^2 $mmol^{-1}$, $\lambda_{max}(\beta\text{-}NO_3^-) = 317$ nm, $\varepsilon_{max}(\beta\text{-}NO_3^-) = 5.7$ cm^2 $mmol^{-1}$. Since the $\Delta_r H^o$ value falls inside the range of the energies of hydrogen-bond breaking and, in addition, $\Delta_r S^o > 0$, it is hypothesized that the $\alpha \rightarrow \beta$ conversion might include the rupture of one hydrogen bond (in the hydration shell) per one $\alpha\text{-}NO_3^-$ entity.

G3

INDIRECT SPECTROPHOTOMETRIC AND ATOMIC-ABSORPTION DETERMINATION OF SOME ELEMENTS BY MEANS OF POLYOXOMETALATES

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Keggin-type heteropolyanions (HPAs) allow to realise indirect determination of P, As and other heteroatoms using ligand atoms. It are discussed existing procedures and proposed a new methods, that can be placed in two groups.

1. Amplification reaction. Method is based on the formation of the 12-molybdo(tungsto)phosphoric acid, its extraction with butyl acetate, stripping and determination of the Mo(W) by means of very sensitive reaction with phenylfluorone in the presence of neonol (polyoxyethylene nonylphenol) ($\varepsilon_{524}=1,68\cdot10^6$). Phosphate or arsenate ions can be determined over the concentration range $2\cdot10^{-8}$ - $2\cdot10^{-7}$ mol/l ($\varepsilon^{524} = 1,67\cdot10^6$). Another method of separation of the excess of molybdate that uses sorption and concentration of HPAs on polyurethanes is worked out.

It is shown possibility of indirect spectropohotometric determination of phosphate without extraction using displacement of equilibrium of $x\mathrm{Mo(R)}_2 + \mathrm{P}\ \Delta\ \mathrm{PMo}_x + 2x\mathrm{R}$ (R = alizarin S, brompyrogallol Red (BPR)) to right side in presence of P. For BPR coefficient of amplification x is equal 9 and effective molar coefficient is $6,7\cdot10^5$. The reaction can be realised on condition that HPA is much more stable than $\mathrm{Mo(R)}_2$. It is very important therefore to use on the first stage micellar solutions of non-ionic SAS. It is shown that HPAs can be concentrated in micelles. Change of the environment from water to organic leads to the increasing of the stability of HPA. Mechanism of interaction and further examples of application of non-ionic SAS in the analytical chemistry of HPAs are discussed.

2. Indirect method of determination of P, As and other elements has been developed using formation of mixed tungstoheteropolyanions $\mathrm{XMeW}_{11}\mathrm{O}_{39}^{q-}$ (Me = Co, Zn) and their separation from excess of metal ions with ion-exchange resin. Co and Zn are determined in effluent by means of spectropohotometry, atomic absorption spectrometry as well as using any other method. In comparison with extraction separation ion-exchange allows to increase number of determined elements and to use other types of HPA including tungsten derivatives.

G4

Some questions of influence of composition of a solution on properties of cellulose

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By the Knudsen effusion method on a mass - spectrometer the thermodynamics of desorption process of the mixed solvent (water - DMSO) in an interval of temperatures 288-357K from cellulose (a degree of polymerization 700, by a crystallinity degree 58 %, fraction 63-100 microns) was investigated. Measurements were made on mass - spectrometer MI-1201 converted for carrying out of the effusion experiments. For reduction of influence of an instrument background by measurements the cell with a heater was located in a trap which is cooled by liquid nitrogen and taking place in volume, having independent spilling system. Presence of the damper, overlapping a molecular bunch, allowed to define the contribution of a background to a useful signal. We shall note, that at closed damper due to presence differentiated spilling volumes of the evaporator and an ionic source the registered instrument background remained constant both at open, and at closed effusion cell. For maintenance of the necessary temperature were used two tungsten -rhenium thermocouples VR 5/20, one of which was placed in the field of a heater, and another is direct in a wall of a cell. Last was used for measurement of temperature of experiment with accuracy 2°, established at calibration on temperature of fusion of silver. The technique of measurement of the humidity, based on integration of the ionic currents registered by a weight - spectrometer, allows to define humidity without extraction of a sample from the device and its weighing.

Before experiment the cellulose material has been humidified with water – DMSO solution. Further repeated measurement of temperature dependences of vapor pressure of water and DMSO with the subsequent drying was carried out. As a result of various vapor pressure components of solvent its structure changed, that has allowed to study system in various conditions.

Preliminary research of systems water - DMSO, cellulose - water, cellulose - DMSO has shown, that the power of interaction water - DMSO exceeds energy of interaction water - water (44 kJ/mole), water - cellulose (37 kJ/mole), DMSO-DMSO (57 kJ/mole), DMSO-cellulose (23 kJ/mole). On seen, it also defines the character of dependences of thermodynamic testimonials from of structure of a mix in system cellulose - water-DMSO.

At interaction of cellulose with a mix water - DMSO, at surplus of water, diffusion of molecules of water in a matrix of cellulose outstrips diffusion of molecules DMSO and the more soassotiates DMSO:2H2O which are formed up to m.f. 0,3. Therefore in this interval of concentration interaction cellulose - water prevails. With increase in DMSOcontents the mix to become more associated owing to intermolecular interaction of its components that results in easing interaction with cellulose. A minimum Δ_{desH} falls XDMSO= 0.65 m.f. Increase in desorption power expenses at X>. 0,7m.f. at small assotiates concentration, caused by deeper penetration of single DMSO molecules into a matrix of cellulose.

Thus, the technique suggested by us allows to receive thermodynamic characteristics of interaction in system polymer - mixed water-organic solvent, thus having allocated influence of each component of the mixed solvent.

G5

LEACHING OF GLAZE ELEMENTS OF HISTORIC CERAMICS TO LIQUID MEDIUM

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In different cultures, the handmade dinnerware, bottles, vessels, jugs and pots prepared from glazed terracotta or ceramics has been traditionally used for daily cooking and storage of food and beverages, frequently alcoholic drink. The glazes provide a hard and non-porous covering on the ceramics body and present different colours for decorating patterns. The main component of this layer consists basically of SiO_2 with relatively high melting temperature ($\approx$1610 °C) however some other oxides PbO, BaO, K_2O, CaO, MgO, Li_2O, Na_2O, FeO, BeO, ZnO, CuO, B_2O_3, MnO, CoO, NiO, Bi_2O_3, are sometimes added in order to decrease the starting temperature of the fusion process during the firing. The most important and frequently used fluxing compound is PbO which has low fluxing temperature; it is approximately 500 °C. The use of lead oxide with high concentration (up to 50w%) in glaze manufacture results in a smooth and shiny effect on the glaze surface. The improper preparation of potteries covered by lead-glaze and their daily use could result in a serious risk for human health since the lead and its compounds are cumulative and highly toxic materials for human body. The lead compounds are accumulated in different human tissues and blood. The origin of the danger is the long-term leaching of lead and other elements from the glaze of terracotta or ceramic dinnerware into acidic food substances. Systematic investigation of leaching of Pb and other elements (Li, Ca, K, Cr, Mn, Fe etc.) into different types of liquid (i.e. 0.01 mol/l citric and tartaric acid solution) stored in glazed potteries were carried out. Long-term kinetics of the leaching effect from 89 pieces of selected pottery items were also measured over a 1-25 days period. Combination of exponential and linear functions with time was found as the best fit to the measured concentration values. The Pb content of the surface layer of glazed potteries was measured by EDXRF analysis with ^{125}I radioisotope excitation and that of the different liquid samples stored in them was determined by ICP-AES method. The concentration values obtained were C_{Pb} = 45 - 50 w% and C_{Pb} = 20 - 200 ppm, respectively. The Pb content and the thickness of the glaze were determined simultaneously with fundamental parameter method. SEM analysis was performed on some glazed terracotta pieces for verification of the quantitative calculation by visualization of result of the leaching process. The highest Pb content measured in the acidic liquid amounted 500 ppm after 5000 minutes leaching time.

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G6

PARTIAL MOLAR VOLUMES AND HEAT CAPACITIES OF $LiClO_4$ AND Et_4NBr SOLUTIONS IN SIX APROTIC SOLVENTS

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This work is concerned with apparent partial molar volumes and isobaric heat capacities of lithium perchlorate and tetraethylammonium bromide in six aprotic solvents of medium to high permitivities, low melting and high boiling points as well as low viscosities. The former salt solutions have had different applications among them the preparation of electrolytic solutions applicable to high energy batteries;[1,2] the second one was chosen here for comparative purposes.

The thermodynamic parameters were evaluated from experimental electrical conductivities and association constants of the solutions, the volumes being obtained from very accurate densities and the heat capacities were determined by micro-calorimetry. All the results were obtained at 25±0.005 °C.

The variation of both apparent molar volumes and heat capacities with ionic strength were analysed through Masson,[3] Redlich and Meyer[4] and Pitzer[5] equations being such variations related to the well known Debye-Hückel limiting slopes from which the corresponding standard partial molar quantities were calculated. Ion-ion, ion-solvent and ion-ion-solvent interactions were related to those gradients.

Where possible specially ionic volumes agree reasonably well with results previously published by other authors.

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Poster presentations

A-P1

Interaction of Dimethylsulfoxide with the Ions Be^{2+} and Cl^-: An Ab Initio Investigation

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ABSTRACT

The interaction of dimethylsulfoxide (DMSO) with the ions Be^{2+} and Cl^- was investigated by quantum chemical methods. Optimal structures of the $Be^{2+}(DMSO)_n$, $Cl^-(DMSO)_n$ (n=1-6) clusters and their binding energies were computed at various level of theory from HF/CEP-31G to B3LYP/6-311G(d,p). The results depended somewhat on the method, indicating that different geometrical arrangements have similar energies. The best calculations (B3LYP/6-311G(d,p)) give a 4+2 shell structure for $Be^{2+}(DMSO)_6$ clusters and a 5+1 shell structure for $Cl^-(DMSO)_6$ clusters. Potential functions for DMSO-Be^{2+} and DMSO-Cl^- were constructed by fitting quantum chemically calculated energies to polynomial functions. A three-parameter analytical function for the DMSO-Cl^- system was found to be in very good agreement with the quantum chemically calculated energies while for the DMSO-Be^{2+} hypersurface an analytical pair potential for use in condensed-phase simulations proved more difficult to generate.

A-P2

A two-dimensional EPR study of copper(II) -β-substituted β-amino acid systems. Steric effects of the substituents on equilibria of metal complexes

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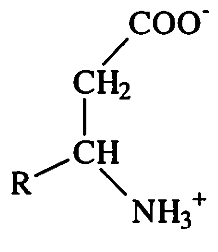

We have studied the complex equilibria of copper(II) with a series of β-substituted β-amino acids (R: H, Me, Et, *i*Bu, *i*Pr, *c*Hex, 1-EtPr and *t*Bu) by pH potentiometry and electron paramagnetic resonance (EPR) spectroscopy. The matrix rank analysis carried out on the EPR spectrum package indicates the formation of 6 independent paramagnetic species. Accordingly, Cu^{2+} (aqua complex) and the complexes $[CuLH]^{2+}$, $[CuL]^{+}$, $[CuL_2H_2]^{2+}$, $[CuL_2H]^{+}$ and $[CuL_2]$ have been considered. In addition, for $[CuL_2]$, two coordination isomers could be identified by the two-dimensional spectrum decomposition method[1]. The formation constants and the EPR parameters have been determined for the above species.

As far as the authors know, this is the first reported case in which a strong correlation has been found between the steric effects of substituents characterized by Meyer's steric parameter[2] V^a and the protonation constants of metal complexes. The observed trend for the preference for non-protonated complexes $[CuL]^{+}$ and $[CuL_2]$ to increase with the bulky of the substituent can be explained by the increasing substituent shielding that hinders the protonation process.

Acknowledgement
We thank the Hungarian Scientific Research Fund OTKA (Grant T-032929).

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A-P3

Ultrasonic relaxation study of triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) in aqueous solutions.

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It is now well established that block copolymers of the type (EO)(PO)(EO) behave in many ways like normal hydrocarbon surfactants [1-3]. The compounds are surface-active and form micelles. In comparison to normal surfactants these compounds have the peculiarity that their CMC and their surface activity depend more strongly on temperature than those for the classic nonionic surfactants.The kinetics of relaxation processes of aqueous solutions triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymers, the Pluronics PE 6400 has been investigated using ultrasonic relaxation method. The ultrasonic relaxation spectra of PE6400 were determined in the concentration range 1-11%. The ultrasonic attenuation measurements in the frequency range 0.1-5 MHz showed the existence of a large excess absorption with respect to water, occurring at concentrations above the CMC of the Pluronic solutions investigated. The ultrasonic spectra show a single relaxation term in the frequency range between 200 kHz and 2 MHz, at the temperature 25^0 C. On this basis we evaluate orders of magnitude values of the rate constant $k^{+}=5\cdot10^{9}\ M^{-1}s^{-1}$ for the copolymer association to, and exit from, its micelles, using the relaxation frequency f_r, and the excess ultrasonic attenuation at different frequency f.

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A-P4

Investigation of structure of liquid 2,2,2 trifluoroethanol: neutron diffraction, molecular dynamics and ab initio quantum chemical study

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Abstract

Molecular conformations and intermolecular H-bonding in liquid 2,2,2 trifluoroethanol (TFE) have been studied by neutron diffraction with hydrogen/deuterium isotopic substitution at room temperature. For comparison, conformations of molecules and their dimers in the gas phase have also been calculated, based on the density functional theory. Energies, geometries and vibrational frequencies of dimers were analyzed. Diffraction data analyzed by MCGR method resulted in a molecular structure in agreement with the findings from gas phase electron diffraction experiments and density functional calculations. The intermolecular structure functions were compared to the same functions from the molecular dynamics simulation. All of the composite radial distribution functions are in good agreement with the simulation results. According to our calculation the hydrogen bonded aggregation size is smaller in pure liquid TFE than in pure liquid ethanol

A-P5

Direct Deconvolution of Femtosecond Kinetic Data

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Ultrafast processes in liquid solutions – like charge and energy transfer, solvation – occur at subpicosecond timescale, and their experimental study is based on femtosecond pump-probe spectroscopy. However, due to the uncertainty relation between the spectral and the temporal widths of the pulses used, selectivity in energy requires pulses not less than a few hundred femtosecond in temporal width. As pulse widths are comparable to characteristic times of the processes studied, severe distortion of the kinetic response function occurs, which can be described by convolution of the instantaneous kinetic response with the correlation of the two pulses.

In this work, we explore the possibility of restoration of the (instantaneous) kinetic response by direct deconvolution, *i. e.*, without any reference to an actual kinetic and/or spectral model mechanism prior to deconvolution. We have examined iterative deconvolution methods in the time domain, as well as inverse filtering methods using Fourier transforms in the frequency domain. Existing deconvolution procedures were modified to work with non-periodic signals and an important experimental noise content, typical of actual femtosecond kinetic data. Tests of the methods were performed on simulated data. The known model functions were then fitted to the deconvolved results, and estimated parameters were compared to the classical "reconvolution" estimates where deconvolution is based on the *a priori* knowledge of the model function.

Deconvolution procedures that gave satisfactory test results were successfully used to analyse measured femtosecond kinetic data of the CTTS reaction of Na^- in tetrahydrofurane.

A-P6

Structural correlations in Alcoholic Aqueous Solutions of Osmium Tetroxide

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The dihydroxylation reaction of olefins by osmium tetroxide to obtain cis-diols is a very important reaction in organic chemistry. Although the reaction can be performed by less expensive and less toxic oxidants such as potassium permanganate, for the asymmetric form of the reaction the yield of the product is higher when osmium tetroxide is employed. The most successful catalytic cycle was obtained by performing the reaction in two separated phases consisting of mixtures of water and tert-butanol.

The identification and structural characterization of all the species involved in a given reaction is crucial to understand the mechanism of the conversion of reactants to products as is a knowledge of the arrangement of the solvent molecules around the molecular species involved. To try to understand the mechanism of the title reaction we have performed an X-ray absorption spectroscopy study in order to determine the in-solution structure of all the species involved in the simplest version of the reaction; only two reactants are involved, and the reaction proceeds in a unique phase. The chosen solvent is a mixture of tert-butanol/water 6 to 1. To obtain information about the arrangement of the solvent molecules around the main reactant, osmium tetroxide, a neutron diffraction study has also been performed. The combination of both sets of data provides a complete picture of the arrangement of the three molecular units, osmium tetroxide, water and tert-butanol, as well as the structure of the species involve in the reaction, from the viewpoint of the metal centre.

A-P7

Kinetics and mechanism of oxidation of hydroxyurea

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Hydroxyurea is an old drug. It was synthesized in 1869 and the inhibitory effect on leukocyte cell growth was first observed in 1928.[i] The clinical use of hydroxyurea as an anticancer agent began in the sixties. More recently, interest was rekindled by the observation that hydroxyurea is also effective in a number of non-plasmatic diseases, including sickel cell anemia and HIV infection.[ii, iii]

The kinetics and mechanism of oxidation of hydroxyurea by potassium hexacyanoferrate(III) in aqueus medium has been investigated using UV-Vis and EPR spectroscopy and was compared to oxydation with dioxovanadium(V) ions. The stocheiometry of the reaction has been determinated spectroscopically. It appears that in both cases hydroxyurea act as two electrondonor.

EPR-spectral measurements indicates that the oxidation of hydroxyurea by potassium hexacyanoferrate(III) or vanadium(V) takes place via a free radical formation followed by its fade. The measured g-value of the radical ($g = 2.0067$) indicates that the unpaired electron is located predominantly at the hydroxamate hydroxyl-oxygen atom.

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A-P8

SPECIATION STUDIES ON VANADIUM(III) – (O,O) OR (N,O) DONOR LIGAND SYSTEMS

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Large number of vanadium compounds have already been synthesized and tested for oral insulin mimetic activity. Stable, neutral, air-resistant, lipophilic but water-soluble V(III) complexes with low toxicity may also serve as insulin-enhancing pro-drugs. Although they would rapidly oxidise *in vivo* to VO(IV) and V(V) at physiological pH, the difference in coordination chemistry of V(III) and VO(IV) or V(V) may lead to fine tuning of hydrophilic/lipophilic balance of the potentially active species to be taken up in the body. This prompted us to explore the interaction between V(III) and some (O,O) or (N,O) donor biomolecules in solution using combined pH-potentiometric and UV-VIS spectroscopic techniques.

Either the (O,O) donor (maltol, tiron and 1,2-dimethyl-3-hydroxy-4(1H)-pyridinone) or the (N,O) donor (pyridinecarboxylic acid) ligands are able to bind V(III) effectively enough to prevent the hydrolysis of the metal ion in the acidic pH range.

With maltol, tiron, the pyridinone derivative, picolinic acid and methylpicolinic acid the formation of 1:1, 1:2 and 1:3 complexes was detected. With methylpicolinate the complex formation started in the measurable pH-range, but parallel hydrolytic processes of V(III) took also place. For picolinic acid the interaction with V(III) shifted into the more acidic pH-range and the formation of MAH_{-1} and MA_2H_{-1} was also detected.

Both dipicolinate and 4-OH-dipicolinate form stable 1:1 and 1:2 complexes with tridentate coordination of their donor atoms below pH 5.

Acknowledgements. The Hungarian Research Fund (OTKA F 32235) is acknowledged for financial support. P. B. acknowledges the Hungarian Academy of Sciences for a János Bolyai Research Fellowship.

A-P9

What can we learn by computer simulations of XAS spectra?

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The work presented in this poster aims to describe DFT based techniques we use to obtain xray absorption spectra and how these computer-simulated spectra can be used to bring in new ideas and interpretations of the experimental data. We have developed methods in order to compute XAS spectra using both MO-cluster and periodic plane-waves based approaches. We present the case of the study of hydrogen-bonded liquid systems such us liquid water[1-3], aqueous solutions[4] of ions or acids, liquids at interfaces[5] and alcohols. Recent experimental developments make it possible to study liquids by mean of O (1s)-core spectroscopies, providing important informations on the local electronic structure of the system under study. However, the complexity and the dynamics of hydrogen-bonded liquids makes it almost impossible to analyze experimental x-ray spectra in great details without the help of theoretical simulations. Simulated spectra can be used to verify validity of theoretical models and contributions.

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A-P10

Excess Molar Volumes and Viscosities of Binary Mixtures of Epichlorohydrin with Alcohols at Different Temperatures

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An excess property of liquid systems, such as excess molar volume (V^E) has been a qualitative and quantitative way of providing information about molecular structure and intermolecular forces in liquid mixtures. Excess volume measurements of binary systems have been widely used to examine theories of liquid- liquid interaction in the mixtures[1-6]. Physical and thermodynamic properties, such as density and excess molar volume of binary systems have been the interest of many researchers (1-2).

Epichlorohydrin (C_3H_5ClO) has been widely employed in chemical industries (for example synthesis of epoxide resins). Very often, it is used together with other chemicals. In the study, we report the volumetric properties of binary systems of epichlorohydrin with methyl alcohol, ethyl alcohol, iso-propyl alcohol and t-butyl alcohol. Experimental data are used to obtain excess molar volume and a new correlation of this property with temperatures and mole fractions.

The densities and excess molar volumes of (epichlorohydrin + alchols) mixtures were determinated at different temperature. The graph of excess molar volumes against mole fracrtion of mixtures shows that the negative and positive slope because of charge-transfer interaction and physical forces at different temperatures, respectively.

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A-P11

Kinetic Model for the HOCl - Cl(III) Reaction

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In order to explore further mechanistic details of the HOCl – Cl(III) reaction, we developed a novel sequential quenched - stopped - flow technique to monitor independently the concentration changes of HOCl, Cl(III) and ClO_2. The method is based on chemically quenching the reaction mixture with 0.6 M NaI solution. The concentrations of the oxychlorine species are calculated from the amount of iodine formed in the quench reaction. Appropriate kinetic traces can be constructed by systematically changing the quench time.[1]

Several kinetic traces were recorded at pH = 1, using various concentration ratios, either in excess Cl(III) and excess HOCl. Chlorine hydrolysis equilibrium may play important role in the kinetics; the equilibrium constant was determined by UV-VIS spectrophotometry.

A simple kinetic model is proposed to explain the features reaction. According to our model Cl(III) does not react directly with HOCl. Instead, it reacts with the more reactive Cl_2 formed from hypochlorous acid. Kinetic traces obtained by numerical simulations reproduces the kinetic features of this system reasonably well.

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A-P12

Kinetic Study of the Osmylation of Olefins by OsO_4

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The coupling of high brilliance 3rd generation synchrotron radiation facilities with stopped flow reaction cell technology has recently begun to open a unique structural window through which one can view millisecond to second timescale chemical reaction processes that occur in the liquid state. Here I will illustrate how the powerful and chemically specific local structure probe, X-ray absorption spectroscopy, is beginning to provide us with new insight into both the electronic and structural aspects of typical reaction processes.

As a case study I will present recent results obtained on the important reaction between osmium tetroxide (OsO_4) and the C=C double bond of simple olefins. With this example I will show how one can extract information on both chemical reaction kinetics and time dependent local structure, and how this information can be correlated with theoretically proposed mechanisms. With the availability of such comprehensive information it may now be possible to gain structural information about short-lived species present during the course of a reaction.

A-P13

INTERACTION BETWEEN NEW DESFERRIOXAMINE B (DFB) MODEL DIHYDROXAMIC ACIDS AND M(II) IONS: EFFECT OF THE COMPLEX GEOMETRY ON THE STOICHIOMETRY OF BIS-CHELATED COMPLEXES

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Polyhydroxamates are often more effective metal ion sequestering agents than the monohydroxamates. This might be one of the reasons, why the natural hydroxamate-based siderophores are polyhydroxamates containing three or in a few cases two chelating moieties. There are, however, several interesting features (e.g. the influence of the length, rigidity or orientation of the linker, relative orientation of the linked chelating groups,...) determining the complex-forming ability of the polyhydroxamates. Both of the connecting chains in the trihydroxamate type DFB have the same special structure, - $(CH_2)_2$-CO-NH-$(CH_2)_5$-, allowing the favoured preorganization of the three chelating functions for the coordination in a mononuclear octahedral complex to iron(III). If however, the length of the linker or the relative orientation of the linked chelating groups is not adequate for the formation of a mononuclear bis-chelated complex, [ML], in that case dinuclear, double-bridged, less stable complex $[M_2L_2]$ is formed. In the present work complexation of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) with six new DFB model dihydroxamic acids ($HO(CH_3)NCO$-$(CH_2)_x$-CO-NH-$(CH_2)_y$-$CON(CH_3)OH$, where the related x,y values are 2,5; 2,4; 2,3; 2,2; 3,4, 3,3, and either the length of the chain or the position of the peptide group is varied) were studied by pH-potentiometric, NMR, UV-VIS and ESI MS methods. According to our results, the stability of the monochelated $[MLH]^+$ complexes formed with these dihydroxamic acids are similar, but in some cases, significant differences in the stability of their bis-chelated complexes can be found. The main conclusion is that the stoichiometry and stability of the bis-chelated complexes depend much more on the geometry of the complex formed than either on the ionic radius of the metal ion or on the length of the linker situating in the studied dihydroxamic acids.

The work was done within the framework of COST D21/01 and supported by OTKA T034674 and Hungarian-Portugal Foundation (TET) P-5/01.

A-P14

Effects of medium and interionic interactions in water-salting solvents

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At studying equilibriums in solutions with formation of associates (complexes) of small and average stability the account of medium effects (inideality) is obligatory. These effects take place and in conditions of a method of the constant ionic environment. However the quantitative account of effects inideality is connected to big enough difficulties, which are aggravated in connection with an opportunity of formation of several complex forms in a solution.

In the present work formation of hydrosulphate - ion HSO_4^- (i.e. only one associate, formation of associates of more difficult composition is excluded) in conditions of a method of the constant ionic medium is investigated. Solubility of strontium sulphate was studied at 25°C in mixes isomolar solutions $NaClO_4$ (or $LiClO_4$) and $HClO_4$, i.e. c by gradual replacement of ions Na^+ (or Li^+) on ions H^+.

The obtained data on solubility $SrSO_4$ are interpreted within the framework of model

$$L^2L_0^{-2} = \exp(-\alpha_0[H^+]) + \beta^{\varnothing}\exp(-\alpha_I[H^+])[H^+] \qquad (1)$$

Where L and L_0- solubility at presence and absence of hydrions in I molar solutions (Na, H)ClO_4 or (Li, H) ClO_4, I-ionic strength of a solution, a $\beta^{\varnothing}$-constant of formation HSO_4^- - in I molar solution $NaClO_4$ (or $LiClO_4$), α_0 and α_I – factors of linear dependence

$$-\ln Ks_0=-\ln Ks_0-\alpha_0[H^+] \qquad \text{and } \ln\beta=\ln\beta^{\varnothing}-\alpha_I[H^+]$$

Equilibrium concentration of hydrions in the majority of experimental points was equated the general concentration $HClO_4$, in view of enough small solubility $SrSO_4$. The opportunity of formation of associate $SrSO_4$ in a solution for the same reason was not taken into account.

The program of the decision of the equation (1) method of nonlinear leastsquares, with a presence of required parameters $\beta^{\varnothing}$, α_0 and α_I and an estimation of their confidential intervals was developed. Dependence $\beta^{\varnothing}$, α_0 and α_I from ionic stregth of a solution is analysed.

A-P15

Evaluation of the action of proteolytic enzymes on the wool fibre by kinetic measurements

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A possible alternative to the classical polluting technologies in textile finishing is the application of biotechnology. Enzymes are used in order to develop an environmentally friendly alternative.

The paper comprise the study of the action of proteolytic enzymes on the wool fibre.

A diffusion study was carried out based on the fluorescence microscopy in order to localize the enzymatic attack into the fibre. During the enzymatic treatment with enzymes a kinetic study was also carried out for a possible evaluation of the enzymatic reaction.

The proteolytic activity of the enzymes using a soluble substrate was determined and their protein contents by the Lowry test.

For the system proteolytic enzymes – wool fibre, the kinetic parameters, Michaelis constant KM and maxim reaction rate Vmax, were measured from the linear regression of the two plots.

The effects of the enzymatic treatment of wool substrate were monitored by using the aminoacid contents of the treatment liquors and the Scanning electron micrographs of wool fibre.

The complex structure of natural fibres, especially of wool fibre complicates enzymatic modification. Thus, the control of the enzymatic reaction is necessary for avoiding the damage of the wool substrate.

A-P16

Complexation of alkali cations by lower rim calix[4]arene tetra(*O*-[*N*-acetyl-*R*-phenylglycine methyl ester]) derivative

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Calixarenes with carbonyl-containing substituents on phenolic groups are effective receptors for alkali and alkaline-earth cations. In calixarene derivatives that possess substituents with both, a hydrogen-bond acceptor (carbonyl group) and a hydrogen-bond donor (*e.g.* –NH– group in secondary amides), circular intramolecular hydrogen bonds are formed which have a strong influence on their ionophoric activity.[1,2]

Complexation of alkali metal cations with 5,11,17,23-tetra-*tert*-butyl-26,28,25,27-tetrakis(O-methyl-D-α-phenylglycinecarbonylmethoxy)calix[4]arene[2] (L) was studied by means of spectrophotometric, conductometric and potentiometric titrations. The solvent effect on the binding ability of L was examined by using two solvents with different affinities for hydrogen bonding, *viz.* methanol and acetonitrile. The stability constants of metal complexes were determined in both solvents. The investigated calix[4]arene amino acid derivative was shown to be an efficient binder for the smaller Li^+ and Na^+ cations in acetonitrile, whereas the bigger Rb^+ and Cs^+ did not fit in the calix[4]arene hydrophilic cavity. The stability of the complexes in methanol was significantly lower which could be explained by different solvation of the cations and by competition between the cations and methanol molecules (*via* hydrogen bonds) for amide carbonyl oxygens. The influence of cation solvation on the complex stability was most pronounced in the case of Li^+ (stability constant of LiL^+ in acetonitrile was quite high, $>10^6$ mol^{-1} dm^3, whereas the one in methanol was low, *i.e.* <10 mol^{-1} dm^3).

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A-P17

A New Bis (3-Hydroxy-4-pyridinonate)-EDTA Derivative as a Chelator for Metal Ions

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The 3-hydroxy-4-pyridinones (3,4-HP) are important chelating agents with several potential applications in medicinal chemistry. Their importance has been mostly associated with the high affinity towards hard trivalent metal ions such as Fe(III), Al(III) and Ga(III), and the potential use as decorporating agents in situations of metal imbalance [1]. Their interaction with divalent species, namely Cu(II) or VO(II) and MoO_2(II), have also been the object of research associated to the inhibition of important biological functions or to the diabetes treatment, respectively [2].

As part of an ongoing project aimed at exploring the polydenticity of 3,4-HP derivatives, a new bis-hydroxypyridonate ligand was prepared, having two of those binding unities coupled to ethylenediaminetetracetic acid (EDTA), via amide linkages, remaining two extra carboxylic groups. This work reports equilibrium studies in aqueous solution for the characterization of this ligand in terms of acid-base properties, the binding affinity towards a set of M^{2+} ions (M = Cu, Ni, Zn), and the estimation of coordination modes. The equilibrium studies are based on potentiometric and spectrophotometric (UV-Vis, NMR and EPR) measurements. The results are discussed based on those reported for mono-hydroxypyridonate derivatives and other relevant analogues.

Acknowledgement: The authors thank to the Portuguese *FCT* (project POCTI/35344/00), the Hungarian-Portuguese Intergovern. program and the COST D21/001 program for financial support.

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A-P18

REACTIVITY STUDIES OF 2-BROMO-2-METHYLPROPANE IN BINARY MIXTURES OF PROTIC AND APROTIC SOLVENTS. CORRELATIONS WITH SOLVENT STRUCTURE

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Due to the increased application of mixed solvents in fields as varied as chemistry, life sciences, industrial processes and environmental protection, structural and dynamic studies in these type of solvents have gone through significant developments in the last years.

In the sequence of recent work on the structural characterization of binary and ternary mixtures of protic and aprotic solvents[1], and in the line of our interest to enlarge the matrix of substrates and solvents used, so that a reliable application of multivariate data analysis can be performed[2], we have been studying the kinetics of some halogenated substrates on mixed solvents.

In this work, we report rate constants for the reaction of 2-bromo-2-methylpropane in the mixtures MeOH/1-PrOH and MeOH/MeCN, for several molar fractions, at 25.00 °C, obtained by a conductimetric technique.

Correlation analysis between rate constants and solvent descriptors, previously determined by us, allowed the identification of the prominent solute-solvent-solvent interaction mechanisms in the rate processes. Further reactivity and mechanistic studies are under way.

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A-P19

RAMAN SPECTROSCOPIC INVESTIGATION OF SPECIATION IN $MgSO_4(aq)$

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Previous Raman investigations on aqueous solutions of $MgSO_4$ have been interpreted either as indicating the presence of contact ion pairs (Davies and Oliver, 1973) or a solvent-separated ion pair (Daly et al., 1972, Rull et al., 1994). However, these studies focused only on the most intensive $\nu_1(SO_4^{2-})$ mode. The present study includes detailed measurements at low wavenumbers (≥50 cm^{-1}), low concentrations, temperatures up to ~200 °C, and in heavy water. The ν_1 mode of $Mg(OH_2)_6^{2+}$ at 358 cm^{-1} develops a shoulder at ~340 cm^{-1} indicative of the penetration of SO_4^{2-} into the inner coordination sphere. In addition a mode at 240 cm^{-1} appears, confirming the presence of the Mg-O-SO_3 moiety. The spectrum of $MgSO_4$ in D_2O supports these spectroscopic assignments and in particular shows that the widely cited interpretation by Rull et al. cannot be correct. Concentration studies of $MgSO_4$ down to concentrations of 0.59 mM show that the mode at 993 cm^{-1}, assigned to contact ion pairs, disappears completely. These findings confirm the results of a recent dielectric relaxation study (Buchner et al., 2003). Raman measurements as a function of temperature show an increase in contact ion pairs with increasing temperature, demonstrating the endothermic nature of their formation.

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A-P20

Solvation Structure of Metal(II) Ions in Nitrogen Donating Solvents

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Solvation structure is most essential and important information to understand the physicochemical properties of the solution containing the metal ion. The solvation structures of the transition metal ions have been investigated mostly in the oxygen-donating solvents, which possess a coordinating oxygen atom.[1] It has been clarified that the bulkiness of the solvent molecule and the positive charge density on the metal ion affect the solvation structure. However, the corresponding structures in the nitrogen-donating solvents are not well investigated, although the electronic donating ability of the solvent is expected to cause the structural change.

In this study, the solvation structures of the transition metal(II) ions were determined by means of the XAFS spectroscopy in a variety of the nitrogen-donating solvents, such as unidentate aliphatic amines like propylamine, bidentate aliphatic amines like ethylenediamine, pyridine and its derivatives, and some nitriles like acetonitrile. The XAFS spectra were recorded in the transmission and fluorescence mode according to the sample concentration at the Photon Factory of the High Energy Accelerator Research Organization. The EXAFS oscillation functions were analyzed using the FEFF-generated parameters, and the structural data around the metal center were determined by the R-space curve fitting in considering the multiple scattering paths.

The bond lengths between the metal ion and the donating nitrogen atoms are changed according to the kind of nitrogen atoms, *i.e.*, aliphatic amines > pyridine derivatives > nitriles, in response to the electronic configuration. The solvation number in unidentate aliphatic amines is decreased due to their strong sigma-donating ability. The steric hindrance around the coordinating site also leads to the reduced solvation number in 2-methylpyridine.

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A-P21

H_2O-D_2O Solvent Isotope Effect on Excess Molar Volumes of 3-Methylpyridine Solutions.

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3-methylpyridine (3MP) dissolved in heavy water exhibits a closed immiscibility loop between 38.5 and 117 °C at normal pressure, while it is completely miscible with water at any concentration and temperature. The purpose of the present investigation is to compare the volumetric characteristics of dilute solutions of 3MP in H_2O and D_2O.

Densities were measured over the concentration range of 0.4 - 4 mole% as a function of temperature between 25 and 45 °C using a vibrating tube densitometer with a reproducibility of $1\mathrm{x}10^{-5}$ g/cm^3. The excess molar volumes for mixtures containing D_2O were found to be more negative than those with H_2O.

>From the densities of the mixtures the partial molar volume of the solute at infinite dilution and the coefficients in the virial expansion of the excess molar volume ($V^e = V_{xx}m^2 + V_{xxx}m^3 + \ldots$) in terms of the aquamolality (*m*, which is the number of moles of solute per 55.508 mol solvent) have been evaluated.

The values of the partial molar volume at infinite dilution were found to be slightly higher (about 0.3%) for the solutions in H_2O than for those in D_2O. The excess volume second virial coefficient (V_{xx}) representing the contribution of solute pairs to the excess molar volume is positive and its temperature dependence shows a characteristic difference between H_2O and D_2O solutions: while the V_{xx}-t curve for H_2O solution is linear in the temperature range covered, that for D_2O solution displays a maximum at about 35 °C.

The observed solvent isotope effect is discussed in terms of solute-solvent and solute-solute interactions.

A-P22

Equilibrium and Structure of the Al(EDDHP) Complex

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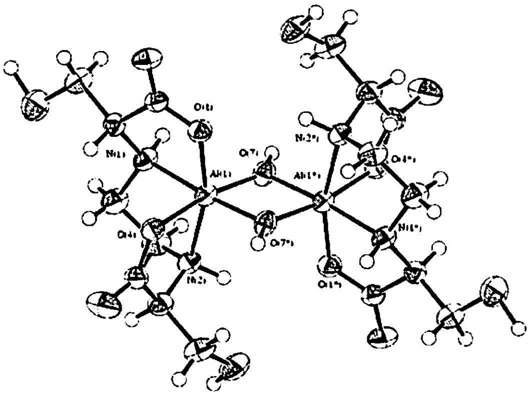
EDTA-type ligands are widely used in industry and analytical chemistry. However there is an urgent need to develop biodegradable analogues of aminopolicarboxylates in order to decrease the environmental impact of these chelating agents. EDDHP (ethylendiamine-N,N'-bis 3-hydroxy-2-propanoic acid) ligand is biodegradable and it forms stable complexes with alkaline earth and transition metal ions.

We report here the results of our pH-potentiometric, ^{1}H and ^{27}Al NMR, study of equilibria (I=1 M KCl, $c_{Al}=5\cdot10^{-3}$ M, $c_L/c_{Al}=1.2$) and X-ray structure of Al(EDDHP) complex. The titrations curves in pH=3-11 could be described with a model consisting of Al^{3+}, $Al(OH)L^0$, $Al(OH)_2L^-$ and $Al(OH)_4^-$.

The ^{1}H NMR spectra of the Al-complex was quite complicated as expected for an inert complex with slow intra-molecular rearrangements. ^{27}Al NMR spectroscopy showed signal of the $Al(OH)L^0$ complex in the 25-30 ppm interval, therefore we concluded that the aluminium forms complex with hexa-coordinated, distorted octahedral structure.

Single crystal X-ray result showed an interesting dimeric structure of $Al_2(OH)_2L_2\cdot2H_2O$.



The $Al_2(OH)_2$ structural motive of $Al_2(OH)_2L_2\cdot2H_2O$ is similar to the $Al_2(OH)_2(NTA)_2^{2-}$ complex, indicating that the hydroxyl oxigens of the 3-hydroxi-2-propionic groups are not coordinated to the inner sphere of the Al^{3+}-ions.

We acknowledge the support of OTKA T 038296 and Nanyo Research Laboratory, Tosoh Co. LTD for donating the ligand.

A-P23

Hydration Structure around the Carboxyl-group Studied by Neutron Diffraction with $^{12}C/^{13}C$ Isotopic Substitution Method

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Time-of-Flight neutron diffraction measurements have been carried out on aqueous 8 mol% sodium acetate solutions in D_2O. The $^{12}C/^{13}C$ isotopic substitution technique has been applied to carbon atoms of the carboxyl-group within the acetate ion in order to obtain information concerning the hydration structure around the carboxyl-group in the aqueous solution.

Neutron diffraction measurements were performed at 25°C using the HIT-II spectrometer installed at the pulsed spallation neutron source (KENS) of the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The first-order difference function[1], $\Delta_C(Q)$, was successfully derived from the numerical difference between scattering cross sections observed for $(CD_3{}^{nat}COONa)_{0.08}(D_2O)_{0.92}$ and $(CD_3{}^{13}COONa)_{0.08}(D_2O)_{0.92}$. The intramolecular contribution within the acetate ion was subtracted from the observed $\Delta_C(Q)$ to obtain the intermolecular difference function, $\Delta_C{}^{inter}(Q)$. The intermolecular distribution function around the carbon atom within the carboxyl-group, $G_C{}^{inter}(r)$ exhibits partially resolved first peak at $r \sim 2.8$ Å, which should involves contribution from D_2O molecules in the first hydration shell. The observed intermolecular first-order difference function, $\Delta_C{}^{inter}(Q)$, was then analyzed by the least squares fitting procedure.

The nearest neighbor $C\cdots D_W$ (D_W: D atom within D_2O) distance and the angle $\angle C\cdots D_W\text{-}O_W$ (O_W: O atom within D_2O) were determined to be $r_{C\cdots D_W} = 2.63(1)$ Å and $\angle C\cdots D_W\text{-}O_W = 120(1)°$, respectively. The coordination number $n_{C\cdots D_W}$ was determined to 4.0(1). These results are in consistent with the structure that water molecules in the first hydration shell of the carboxyl-group, are hydrogen bonded with oxygen atoms of the carboxyl-group. The present value of $n_{C\cdots D_W}$ is in good agreement with that obtained from our previous X-ray diffraction study.[2]

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A-P24

Newly Developed Solution X-Ray Diffractometer Using CCD Detector and Its Application to Studies on Liquid Structure

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A solution X-ray diffractometer using a CCD (charge coupled device) detector has been developed. Characteristic X-rays were generated from a rotating Mo anode. Mo Kβ radiation was eliminated by a graphite crystal monochromator and Mo Kα line was used for transmission measurements. The camera length was 10.7 cm. The effective area of CCD is 94.4 mm × 94.4 mm (pixel size is 0.082 mm) and small. In order to cover the scattering angle 2θ of 2° - 140°, the angular range was divided into four blocks. Intensity measurement without irradiation in a certain block was needed for the correction of background. Measurements should be repeated twice in order to avoid irregular noise due to cosmic rays. Thus, the total irradiation time is 50 min and this is similar to a case using an IP (imaging plate) detector. Two-dimensional data on CCD were quickly transferred and stored in a microcomputer. On the other hand, data on IP should be read by measuring luminescence intensities stimulated by laser beam. The total time necessary before data analyses is shorter in the present CCD system. Two-dimensional data were integrated to give one-dimensional data and the resulting data were corrected for cell scattering, polarization, absorption, multiple scattering and Compton scattering by a usual way.

Benzonitrile and *N,N*-dimethylformamide were measured by the present CCD system and a usual θ-θ type diffractometer. The reduced intensities and radial distribution functions obtained by the two methods agreed well within experimental uncertainties.

Liquid structures of acetonitrile, propionitrile, acrylonitrile and benzonitrile are compared and discussed.

A-P25

About the elasticity of the spatial H-bond network in liquids

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The elasticity of the spatial H-bond network in liquids is presented as a module of an all-round compression, e.g. the reverse value of the isothermal compressibility. The elasticity of the spatial H-bond network in diamines, diols, aminoalcohols, as well as of light and heavy water was calculated. The calculations were based on the experimental data for the isothermal compressibility received by the precision instrument of the all-round compression for all of the above-mentioned solvents. The reverse dependence of the network elasticity on the number of the network's three-dimension defects was demonstrated.

The comparison with the isothermal compressibility and the module of all-round compression (the elasticity) of liquids without the spatial H-bond network, such as liquid alkanes, aliphatic alcohols, benzene and carbon tetrachloride was carried out.

The elasticity of the diamines, diols and aminoalcohols is 4 times higher than that of the liquid alkanes, and 2 times higher than that of the aliphatic alcohols. It is explained by the fact that diamines, diols and aminoalcohols have the spatial H-bonds network. It is highly probable that in this case the spatial network is a determining factor in spite of the fact that other interactions are present in those liquids. That is why the elasticity of diamines, diols and aminoalcohols dramatically differs from the elasticity of aliphatic alcohols and liquid alkanes, and has the opposite dependence from the length of the hydrocarbon bridge in the molecule (the bridge plays the role of the network defect).

Study was supported by Russian Foundation of Fundamental Research (project № 03-03-32836).

A-P26

The formation of Rh(I)-carbonyl complexes with water soluble phosphine ligands and their hydrogenation reactions in aqueous media

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The rhodium complexes with water soluble phosphine ligands are very important catalysts of alkene (e.g. propene) hydroformylation. In the Ruhrchemie-Rhône Poulenc process[1] of propene hydroformylation the key to the success is the highly hydrophilic catalyst: [HRh(CO)(*m*TPPTS)$_3$]. The same complex is also effective for 1-octene hydroformylation, but its activity depends on the pH of the aqueous phase[2]. Our previous results[3] using [RhCl(CO)(mTPPMS)$_2$] (*m*TPPMS=*meta*-mono-sulphonated triphenylphosphine, sodium salt) precursor showed, that the formation of the active hydrido-carbonyl complex [HRh(CO)(*m*TPPMS)$_3$] is strongly promoted in alkaline solutions.

We report the first successful preparation of [Rh(OOCCH$_3$)(CO)(mTPPMS)$_2$] and the study of its hydrogenation in aqueous solution; the results are compared to those obtained with the chloro-carbonyl complex. The key step of the preparation is the complete halide removal. According to the pH-metric and NMR results, in neutral and alkaline solutions the acetato- and chloro-complex[3] reacted similarly in hydrolysis and in hydrogenation to [HRh(CO)(*m*TPPMS)$_3$]. However, in the acidic range their properties are different, due to the protonation of the labile acetate group.

Acknowledgement: The authors thank the financial support by the Hungarian National Research Foundation (OTKA F037358).

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A-P27

Excess Molar Volumes and Refractife Indexes of Binary Mixtures (Epichlorohydrin + Acetone and Epichlorohydrin + Chloroform)

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The most important feature of epichlorohydrin is different reactivity of the various compounds containing epoxide. Epoxidation of unsaturated compounds is usually carried out in the industry. For example, application of aqueous peracetic acid for the epoxoidation of vegetable oils to manufacture epoxy stabilizer for PVC has become a common process (1).

An excess property of liquid systems, such as excess molar volume (V^E), excess molar refractive indexes, etc. have been a qualitative and quantitative way of providing information about molecular structure and intermolecular forces in liquid mixtures. Excess molar volume measurements of binary systems have been widely used to examine theories of liquid- liquid interaction in the mixtures. Physical and thermodynamic properties, such as density and excess molar volume of binary systems have been the interest of many researchers (2).

We were investigated to the excess molar volumes and refractive index of binary mixtures (epichlorohydrin + acetone, or + chloroform) at room temperature and atmospheric pressure. The excess molar properties of binary mixtures (epichlorohydrin + acetone or + chloroform) were explained by the chemical and physical forces such as charge-transfer complexes, molecular interaction, etc.

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A-P28

Apparent molar volumes of divalent transition metal perchlorates and chlorides in N,N-dimethylacetamide

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The apparent molar volumes of perchlorates and chlorides of the Mn(II)-Zn(II) series, as well as for the isomolal $M(ClO_4)_2$-MCl_2 mixtures in N,N-dimethylacetamide were determined.

V_Φ against $c^{1/2}$ plots for all salts were found to be linear over the concentration range studied. Therefore, the Masson's type relation for these salts was valid and the apparent molar volumes were obtained from the linear extrapolation.

It was found that the variation of the partial molar volumes of the divalent metal cations solvated with N,N-dimethylacetamide within Mn(II)-Zn(II) series is as follows:

$$V^o_\Phi[Mn^{2+}] > V^o_\Phi[Co^{2+}] \approx V^o_\Phi[Ni^{2+}] < V^o_\Phi[Cu^{2+}] > V^o_\Phi[Zn^{2+}].$$

It is related to the fact that the factors controlling the coordination state of the metal perchlorates are size and shape of the solvent molecules and the nature of the central metal ion.

The values of V_Φ^o for perchlorate – chloride pairs are much the same at 25°C (almost within the experimental error limits). It seems to indicate that the coordination state of MCl_2 in DMA solution is similar to that of $M(ClO_4)_2$. However, considerable differences between volumetric properties of N,N-dimethylacetamide solutions of respective perchlorates and chlorides are observed in case of concentration dependence of the apparent molar volume and temperature dependence of the limiting apparent molar volume. These differences observed are interpreted in terms of formation of the respective chloride-complexes of the divalent transition metal cations.

A-P29

Complex formation of copper-, cobalt and nikkel salts in ethylene glycol as a solvent

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Following our studies in the field of metal complexes of ethylene glycol (e.g. [1, 2]), the solvating property of the ethylene glycol was investigated. Different copper-, cobalt and nickel salts (chloride, nitrate and perchlorate) were chosen as metal salts and the spectrophotometry and the ESR spectroscopy were used as an experimental methods. The experimental data and the conclusions were compared with solvating properties of different non-aqueous solvent (acetonitrile, acetone, ethanol, dimethyl sulfoxide) against the same salts.

The measurements were performed in mixture of water and ethylene glycol and in pure eth0ylene glycol. The ratio of metal ion to anion (chloride, nitrate and sulfate) was changed and UV and Visible spectrums, ESR spectrums were recorded. Graphical and computing calculation methods were used to determine stability constant of complexes or solvates.

On the basis of the results, it could be concluded that the ethylene glycol prefers the formation of ion pairs, especially in the case of the chloride salts. Nevertheless, the complex formation processes are the same, than in other non-aqueous solvent.

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A-P30

THE HYDROPHOBIC HYDRATION IN AQUEOUS SOLUTIONS OF ALKALI METAL PROPIONATES.

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In this work the effect of the hydrophobic hydration of anions is investigated on the example of aqueous solutions of alkali metal propionates. The study of the molecular-kinetic mobility of water molecules in aqueous solutions of potassium and cesium propionates was carried out by the method of the microwave dielectric spectroscopy. The measurements of the high-frequency dielectric permittivity and losses were fulfilled by the method of thin dielectric rod in the wave-guide at 7 – 25 GHz, in wide area of concentrations at temperatures 288 - 308K. The dispersion of the complex dielectric permittivity in the investigated systems at all temperatures and concentration of salts is described by the Cole-Cole equation. The dielectric relaxation time τ and enthalpy $\Delta H_{\varepsilon}^{++}$, that characterized the mobility of water molecules in the solution H-bond net were calculated. These parameters for solutions of potassium and cesium propionates were compared with data at carboxylate raw of salts (potassium and cesium acetates and formates). The decrease of τ and $\Delta H_{\varepsilon}^{++}$ of potassium and cesium formate solutions testifies to breaking of H-bond net of water. The growth of τ and $\Delta H_{\varepsilon}^{++}$ of potassium and cesium propionate solutions indicates the structure-making influence of anions on the tetrahedral hydrogen bond net of water. Propionate and formate ions have identical polar groups but different non-polar parts. The changes of τ in solutions show that the strong H-bonds between molecules of water and formate ions results in breaking of the tetrahedral H-bonds net of water. Therefore increase of τ and $\Delta H_{\varepsilon}^{++}$ is determined by influence of the non-polar part of $C_2H_5COO^-$ ion. So, the propionate anion is hydrophobic hydrated.

This work was supported by the Russian Foundation for Basic Research, no. 01-03-32041, MAS no. 03-03-06234.

A-P31

STUDIES OF BISMUTH TRIFLUOROMETHANESULFONATE SOLUTION IN *N,N*-DIMETHYLTHIOFORMAMIDE

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Due to relativistic stabilization of the $6p_{1/2}^2$ pair bismuth exists in the uncommon oxidation state +1, however, the Bi(I) cation is unstable in aqueous solution[1]. The aim of the present work was to study stable species with bismuth in low oxidation states, and for this reason we have investigated *N,N*-dimethylthioformamide (DMTF) solutions of dissolved bismuth trifluoromethanesulfonate ($Bi(OTf)_3$). Previously, it was found that DMTF solvent stabilised lower oxidation states of the metal cations[2]. Upon dissolving anhydrous $Bi(OTf)_3$ in DMTF yellow-red solutions were obtained[3]. EXAFS studies have shown that one S atom in DMTF molecule coordinates two Bi ions with a mean Bi-S bond distance of 2.54 Å. In VIS spectra the maximum of absorption was observed at 457 nm. IR spectra of the solution were recorded and compared with the spectra of DMTF solvent[4]. The Bi-S stretching vibration appears at 289 cm^{-1}, similarly as for other metal solvates with the same ligand[2]. In the reduction half-cycle of the voltammetric curve we observed two partially overlapping maximas, what indicates that in this system, Bi may appear in two oxidation states: +1 and +3. However, structural studies showed the equivalence of both Bi-S bonds in the dimer suggesting the formation of a resonance structure with both Bi ions with the average oxidation state +2.

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A-P32

Modelling of Cu-AMPSO-OH system and refinement of stability constants by polarographic and potentiometric optimization tools

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Copper binding properties have been investigated for several popular zwitterionic buffers. Amongst them, it is expected that strong copper complexes of the biological buffer 3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid (AMPSO) would be formed in systems containing copper ions when this buffer is used to control the pH.

In this work, the behaviour of solutions containing AMPSO and copper(II) was studied by two analytical techniques, glass electrode potentiometry (GEP) and direct current polarography (DCP), at fixed total AMPSO to total copper(II) concentration ratios ($[L_T]:[M_T]$) and various pH values, at 25 ºC and ionic strength 0.1 M KNO_3. The $[L_T]:[M_T]$ ratios used were 9.1 ($[Cu] = 9.44 \times 10^{-4}$ M), for GEP, and 155 ($[Cu] = 4.9 \times 10^{-5}$ M), for DCP. The predicted model (CuL^+, $CuL(OH)$, CuL_2, $CuL_2(OH)^-$, $CuL_2(OH)_2^{2-}$ and CuL_3^-), and its overall stability constants, was obtained by combining the results of both electrochemical techniques. Five of these complexes [$CuL(OH)$, CuL_2, $CuL_2(OH)^-$, $CuL_2(OH)_2^{2-}$ and CuL_3^-] are reported for the first time.

Acknowledgement: Financial support by FCT from Portuguese Government, Project POCTI/39950/QUI/2001, is gratefully acknowledged.

A-P33

Solid-Liquid Phase Diagrams of Some Salt Hydrate Mixtures

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Solid-liquid phase diagrams were obtained from cooling curve measurements on melts of mixtures of $Mg(NO_3)_2{\cdot}6H_2O$ (**MgN**) with $Mg(CH_3CO_2)_2{\cdot}4H_2O$ (**MgA**) and with $Al(NO_3)_3{\cdot}9H_2O$ (**AlN**) and of $NH_4Al(SO_4)_2{\cdot}12H_2O$ (**AAl**) with NH_4SO_4 (**AS**) and with $Al_2(SO_4)_3{\cdot}nH_2O$ (n = 16 to 18) (**AlS**). In mixture **MgN+MgA** a congruently melting compound $[Mg(CH_3CO_2)_3(H_2O)_2]NO_3$ was found,[1] as well as a low-melting phase at a ratio of 2 **MgN** : 1 **MgA** in the diagram, with eutectics at both its sides. In mixture **MgN+AlN** the diagram differed from that by Mokhosoev and Got'manova[2] for this system, having a much deeper minimum and at a higher x_{AlN}. Mixture **AAl+AS** showed the formation of a peritectic at a mole fraction $x_{AS} > 0.45$ and a broad minimum in the phase diagram at $x_{AS} > 0.6$. In mixture **AlA+AlS** a eutectic was found at $x_{AlS} = 0.32$.

It was attempted to model the **MgN+AlN** system up to $x_{AlN} = 0.4$ by the BET method,[3] according to which the liquidus temperature, T is given by:

$$\ln[a_S(T,x)a_W^{j}(T,x)] - \ln[a_S(T_m,1)a_W^{6}(T_m,1)] = \{L_j - H_S^E - 6H_W^E\}/R\,[1/T - 1/T_m]$$

where x is the composition (x_{AlN}) at which T applies, L is the molar enthalpy of fusion of S = MgN, W = H_2O, $j = 9x_{AlN} + 6(1-x_{AlN})$, and the excess enthalpies, H^E, are obtained from the BET method, by which the salt and water activities a are calculated. Thus, for **MgN** the BET parameters are $r = 4.92$ and $c = 107$, $L = 38.5$ kJ/mol, hence, $\{L - H_S^E - 6H_W^E\}/R = 3702$ K and $\ln a_S(363,1)a_W^6(363,1) = 26.06$. Iteration is carried out until a temperature T is found that equates both sides. Agreement with the present phase diagram and with that of Mokhosoev and Got'manova[2] is obtained with assumed BET values for **AlN**: $r = 11$ and $c = 9.4$ and 8.4, respectively.

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A-P34

Solubility of potassium hydrogen phthalate in potassium chloride solutions

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The salt potassium hydrogen phthalate has been intensively used in pH determinations as its 0.05 mol kg^{-1} solution was selected as a primary standard (1). The assignment of pH to this standard, as well as to other buffers, requires the preparation of solutions to which small portions of potassium chloride are added (1). If the concentration of this salt is increased, it may cause precipitation of potassium hydrogen phthalate due to its low solubility. For this compound, only a few solubility data were found in the literature (2,3).

In this work, solubility curves for potassium hydrogen phthalate have been determined, in the temperature range 5 to 60 °C, at 5 °C intervals, in water and in potassium chloride solutions at various molalities.

The experimental measurements were carried out by the equilibrium method (4) and the amount of solute in the satured solutions was determined gravimetrically.

At 25 °C, the solubilities of potassium hydrogenphthalate in water and in a 2.7 mol kg^{-1} KCl solution were found to be 0.55 mol kg^{-1} and 0.078 mol kg^{-1} , respectively.

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A-P35

Dimethylsulfoxide solvates of the trivalent Al, Ga, In, and Tl ions.

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EXAFS measurements on the dimethylsulfoxide solvated gallium(III), indium(III) and thallium(III) ions in solution display similar M-O bond distances as in the solid solvates. All trivalent group 13 metal ions (M = Al, Ga, In and Tl) coordinate six dimethylsulfoxide molecules in solution and in solid solvates, while the coordination number of the solvated group 3 metal ions, Sc(III), Y(III) and La(III), increases with increasing ionic radius.[1] The M-O-S angles decrease from 133° for the $Sc(dmso)_6{}^{3+}$ solvate to 121° for $Tl(dmso)_6{}^{3+}$ in the solid state, and is as low as 116° for the isoelectronic $Hg(dmso)_6{}^{2+}$ solvate, reflecting increasing covalency in the metal-oxygen bonding character.[1,2] The M-O-S angles for $M(dmso)_6{}^{3+}$ ions, M = Ga, In and Tl, in dimethylsulfoxide solution are 129(1), 125(1) and 124(2)°, respectively. For isostructural solid compounds with solvated $M(dmso)_6{}^{3+}$ ions the octahedral MO_6 coordination entities are increasingly compressed along one threefold axis with increasing size of the trivalent ions M = Al, Ga, In, and Tl, respectively. For $Tl(dmso)_6{}^{3+}$ ions in dimethylsulfoxide solution the disorder parameter of the M-O bond is about twice as large as for the solid and indicate an anomalously large spread in the Tl-O bond distances.[2] Similar effects were previously observed for the isoelectronic mercury(II) ion, and can be interpreted as dynamic disorder due to vibronic mixing of electronic states with close energy levels, a weak pseudo-Jahn-Teller effect.

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A-P36

Thermodynamics of the Liquid-phase Ferro-ferrisulphate Environmentally Safe Redox-process of Hydrogen Sulphide-containing Gas Processing

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Thermodynamics research of the liquid-phase processes of the hydrogen sulphide-containing gas processing introduces an important problem with an aim of creation of wasteless or low-waste technologies in many fields of industry.

The present work has studied the liquid-phase ferro-ferrisulphate redox-process, based on usage of the following reactions (with regeneration of oxidant by chemical or electrochemical methods):

$$H_2S_{gas} + Fe_2(SO_4)_{3\,aq} = S_{rhomb} + 2FeSO_{4\,aq} + H_2SO_{4\,aq}; \qquad (1)$$

$$4FeSO_{4\,aq} + 2H_2SO_{4\,aq} + O_{2,\,gas} = 2Fe_2(SO_4)_{3\,aq} + 2H_2O_{aq}; \qquad (2)$$

$$2H^+ + 2\,e^- = H_{2,\,gas}\ \text{(process on the cathode)}; \qquad (3)$$

$$Fe^{2+}_{aq} - e^- = Fe^{3+}_{aq}\ \text{(process on the anode)}. \qquad (4)$$

The studying of the reaction of H_2S_{gas} oxidation by the solution of Fe(III) sulphate has been carried out in isoperibolic calorimeter of dissolution. The enthalpy of the reaction (1) is found out and on its basis with the usage of reference data on the entropy of the initial and reaction substances the temperature relation of Gibbs energy and the equilibrium constant of the hydrogen sulphide oxidation process were obtained. The prospects of the ferro-ferrisulphate process usage are shown both with thermodynamical and technological points of view. Thus, the precipitation reaction of sulphur by Fe(III) sulphate solution even at 373 K remains practically irreversible. And the regeneration of the waste solution by chemical or electrochemical methods that do not influence on environment negative impact is possible.

A-P37

Selectivity Change of Water to Cobalt(II) Ion in Binary Mixtures of Water and Aprotic Solvents with Strong Donor Properties

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Water is a protic solvent with extensive hydrogen bonding (relative dielectric constant ε(water) = 78.54[1]; donor number D_N(water) = 18.0[2]; acceptor number A_N(water) = 54.8[2]). *N,N*-Dimethylformamide (DMF), 1,1,3,3-tetramethylurea (TMU) and hexamethylphosphoric triamide (HMPA) are aprotic donor solvents. Some of their solvent properties are as follows; ε(DMF) = 36.71, ε(TMU) = 23.6, ε(HMPA) = 29.3[1] ; D_N(DMF) = 26.6, D_N(TMU) = 31.0, D_N(HMPA) = 38.8[2] ; A_N(DMF) = 16.0, A_N(HMPA) = 10.6[2] . The solvation structure of cobalt(II) ion in water and DMF is six-coordinate octahedral[3]. In bulky solvents, such as TMU and HMPA, the solvation number is reduced for relaxation of the sterically repulsive interaction around the central metal ion, and cobalt(II) ion has a four-coordinate tetrahedral structure[4, 5]. The solvation structures of cobalt(II) ion in binary mixtures of water and these strong donor solvents have been determined by means of EXAFS (extended X-ray absorption fine structure) and electronic spectroscopy.

In water-HMPA and water-TMU solvent mixtures, an octahedral – to - tetrahedral structure change took place in the ranges of 0.6 to 0.8 mole fraction of HMPA and 0.9 to 0.94 mole fraction of TMU, respectively. Preferential solvation of water was seen in hexasolvated cobalt(II) ion, while HMPA and TMU selectively coordinate to tetrasolvated cobalt(II) ion. In water-DMF mixed solvents, cobalt(II) ion was preferentially solvated by DMF in the ranges of 0 to 0.6 mole fraction of DMF, while solvated by water in the ranges of 0.6 to 1 mole fraction of DMF.

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A-P38

Activity coefficients of hydrochloric acid in the system $HCl + CH_3CO_2H + H_2O$

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The activity coefficient of neutral species in aqueous solutions is often assumed to be close to 1 and ignored in calculations of equilibrium constants, because the departure from ideal behaviour is mainly attributed to electrostatic forces between ions. Nevertheless specific interactions between charged and uncharged particles have to be taken into consideration when solutions are not dilute and accurate determinations are required[1].

The presence of acetic acid (HAc) molecules in hydrochloric acid aqueous solutions will certainly alter the activity coefficient of this acid and the study of this influence is the aim of the present work.

Activity coefficients of HCl have been determined in solutions of both acids with varying composition and ionic strength, up to 2 mol kg^{-1}, from potentiometric measurements on galvanic cells without liquid junction, in which a commercial glass electrode (Methrom, 6.0133.122) and silver, silver chloride electrodes were used. These were prepared in the laboratory, as described in the literature[2].

The Pitzer formalism was applied to this system and a sum of the parameters realated to interactions between the acetic acid molecule and the Cl^- and H^+ ions was evaluated at each ionic strength.

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A-P39

Thermodynamic and Transport Properties of Aqueous tri-Sodium Citrate System at 298.15 K

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Sodium citrate is an important organic salt in biotechnology, pharmaceutics and agriculture. Thermodynamic properties such as activity and molar volume and transport properties such as viscosity are needed to industrial equipment design.

In this work new measurement of the isopiestic water activity, density and viscosity of aqueous tri-sodium citrate system ($C_6H_5Na_3O_7$) are obtained at 298.15 K. The parameters of the Pitzer ion-interaction model are evaluated from isopiestic data. We also compared the apparent molar volume at infinite dilution of group contribution method for $C_6H_5Na_3O_7$ (aq) to our result evaluated from experimental density data. The experimental viscosity data have been fitted to the Kumar and Jones-Dole equations. The Kumar equation parameters h and B, and ion-ion and ion-solvent interactions by the least square method were obtained for this system.

A-P40

Electrolytic conductance of aqueous solutions of lithium, sodium and potassium cyclohexylsulfamates

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The conductance of lithium, sodium and potassium cyclohexylsulfamate in water was determined up to the concentration of 0.10 mol dm^{-3} and in the temperature range from 298.15 K to 338.15 K. The investigated salts behave as strong electrolytes. The molar conductivity at infinite dilution as well as the Onsager limiting slope were calculated. Both parameters depend on the size of the cation and temperature. The association constants between ions were determined by a method described by Ives using a stepwise extrapolation procedure. The association constant was found to decrease with increasing size of the cation. From the temperature dependence of the association constant the enthalpy and entropy of the association process were calculated. The Gibbs free energy of association of the investigated ions is negative, their value increasing with decreasing cation size. The enthalpy for the association process is, within experimental uncertainities, equal to zero, while the entropy is positive and decreases with increasing size of the cation. The association constant was also calculated with the sphere-in-continuum model in which ions are regarded as hard spheres immersed in a continuous medium. Agreement with the experimentally determined association constant is relatively good.

A-P41

Hydration Structure around the Methylene-group of Glycine Molecule

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Neutron diffraction measurements on H/D isotopically substituted aqueous 4 mol% glycine solutions have been carried out in order to obtain structural information on the hydration shell around the methylene-group of glycine molecule in the partial structure function level.

Neutron diffraction measurements for sample solutions, I $(ND_2CD_2COOD)_{0.04}(D_2O)_{0.96}$, II $(ND_2CH_2COOD)_{0.04}(D_2O)_{0.96}$, III $(N^{0}H_2CD_2COO^{0}H)_{0.04}(^{0}H_2O)_{0.96}$, and IV $(N^{0}H_2CH_2COO^{0}H)_{0.04}(^{0}H_2O)_{0.96}$ (^{0}H: H/D = 64/36, $b_H = 0$), were performed at 25 °C using ISSP 4G diffractometer installed at JRR-3M research reactor in Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. The incident neutron wavelength, $\lambda = 1.104 \pm 0.005$ Å, was employed. Scattered neutrons were collected over the angular range of $3 \leq 2\theta \leq 115°$, corresponding to $0.30 \leq Q \leq 9.60$ Å^{-1} ($Q = 4\pi\sin\theta/\lambda$). The details of the hydration structure around the methylene-hydrogen atoms were deduced from the partial structure factors, $a_{H_MH_{ex}}(Q)$ and $a_{H_MX}(Q)$, (H_M: methylene hydrogen, H_{ex}: exchangeable hydrogen, and X: O, N, H_M, and C atoms, respectively) which were derived from the combination of observed first-order difference functions[1], $^{D}\Delta_H(Q)$, between cross sections for samples I and II, and $^{0H}\Delta_H(Q)$, between those for samples III and IV, respectively. Structure parameters for the first hydration shell around the methylene-hydrogen atom, were determined from the least squares fitting analysis of observed $a_{H_MH_{ex}}(Q)$ and $a_{H_MX}(Q)$ functions.

The nearest neighbor $H_M \cdots O_W$ (O_W: water oxygen) and $H_M \cdots H_W$ (H_W: water hydrogen) distances were determined to be 2.64(1) and 2.87(1) Å, respectively, suggesting that water molecules in the first hydration shell take some preferred orientation. The present value of the coordination number, $n_{H_M \cdots O_W} = 0.86(3)$, implies that ca. 2 water molecules are involved in the first hydration shell around the methylene-group of the glycine molecules.

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A-P42

Excess Properties of Binary Mixtures of 1-Methyl-2-pyrrolidinone with Water or Water-d_2

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This work is continuation to our systematic study of deuterium isotope effects on thermodynamic properties in binary mixtures of water with various dipolar aprotic solvents.[1,2] Dipolar aprotic compounds as the organic component in binary aqueous mixtures are interesting for example because of their solvent effect on rates of reactions.[3] Many of them, like 1-methyl-2-pyrrolidinone (NMP), are also versatile solvents in various industrial processes. Excess properties of binary mixtures of H_2O with NMP have been reported in the literature quite extensively. However, studies on the properties of corresponding systems containing D_2O instead of H_2O do not exist.

In the present work densities and refractive indices of binary mixtures of H_2O or D_2O with NMP have been measured over the entire mole fraction range at temperatures from 278.15 K to 318.15 K. A Sodev 03-D vibrating-tube high precision densimeter, operated under the static mode, was used in the density measurements and an Abbe type ATAGO 3T refractometer in the refractive index measurements. Molar volumes, excess molar volumes, partial molar volumes, excess partial molar volumes and their derivatives with respect to temperature were calculated from the results of density measurements. Various mixing rules for the refractive indices in the mixtures were applied to predict the excess molar volumes from the refractive index measurements.

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A-P43

A Detailed ^{27}Al-NMR Spectroscopic Study of Aqueous Solutions Containing $Al(OH)_3$ and MOH ($M^+ = Na^+, K^+$ and Li^+)

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^{27}Al NMR spectra were recorded at room temperature for an extensive series of aqueous MOH solutions ($M^+ = Na^+$, K^+ and Li^+) with total aluminium concentrations of $0.005\ M \leq [Al(III)]_T \leq 3\ M$. All spectra exhibited only a single peak. In NaOH, at $[Al(III)]_T \leq 0.2$ M), the chemical shift changed systematically upfield with increasing $[NaOH]_T$. In solutions with $[Al(III)]_T \geq 0.8$ M no such variations were observed. The chemical shift variations were more pronounced in LiOH but were absent in KOH solutions. The integrated intensities display systematic variations, with an increasingly significant fraction 'missing' at high $[Al(III)]_T$, which is indicative of speciation changes. Systematic variations in the viscosity-corrected linewidths, which parallel the changes in the integrated intensities, support the existence of speciation changes. The 'missing' intensity was consistent with the formation of a dimeric aluminate species that has also been identified by Raman spectroscopy. The chemical shift variations on the other hand are consistent with an octahedral species, presumably $Al(OH)_6^{3-}$. However, no ^{27}Al-NMR signal corresponding to such a species was observed and its existence could not be unequivocally proven from the ^{27}Al-NMR measurements alone.

A-P44

EFFECT OF COMPETING HYDRATION AND SOLVATION ON SOLID PHASE FORMATION IN SALT – H_2O – DMSO SYSTEMS

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In our research group for many years the systematic study of the effect of competing interactions in solutions on the properties of liquid and solid phases was carried out. Some regularities of the solid phase formation in the ternary aqueous systems where hydration, ionic association and acidocomplexation play the leading role were revealed. In this work we present some results of the study of solid phase formation in the systems "salt – water – organic solvent".

The systems containing the cations with different coordination ability (Cu^{2+} and Cd^{2+}) in presence or absence of acidoligand (Cl^- and SO_4^{2-} as the anions) were chosen for the investigation. The study of these systems enables us to draw the next conclusions:

- The crystallization of mixed water-dimethylsulfoxide crystallosolvates is observed in the systems under study except $CuSO_4$ – H_2O – DMSO;
- The softer is the central cation (Cd^{2+} > Cu^{2+}) the more preferable is its solvation by dimethylsulfoxide;
- The formation of acidocomplexes $CuCl_x^{2-x}$ promotes the coordination of dimethylsulfoxide molecule by the copper ion.

The results are discussed in terms of hard and soft acid and bases theory.

Russian Fund of Basic Investigations (grant 02-03-32729) and Program "Universities of Russia" (project UR. 05.01.004) are thanked for the financial support.

A-P45

UV-Vis Spectroscopy Study of Enzymatic Solution in Textile Finishing

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Sustainable development imposed the application of new, clean technology. Accordingly the use of enzymes in textile industry seems a good solution for the replacement of the classic polluting processes. Enzymes are one of the best catalysts having a high regio- and stereo-selectivity. Working in mild conditions, enzymes insure a save of energy diminishing the *green house* effect.

In textile field enzymes have many possible applications starting with the raw material work-up (desizing of cotton, retting of flax and wool carbonization). The enzymatic finishing has now a succeeds in a number of processes in cotton finishing like: bio-polishing, bio-stoning, etc. many attempts have been done for applying biotechnology for wool finishing as well as for synthetic fibers finishing technology.

One of the problem in connection with enzyme applications in textile work-up is the reaction control. The monitoring of the enzymatic reaction is absolutely necessary for avoiding the damage of the textile materials. Thus, the application of UV-Vis spectroscopy for controlling the textile reaction with enzymes is presented in the case of proteolytic action on wool as substrate.

A-P46

Coordination Chemical Application of FTIR-, Raman-, Mössbauer spectroscopies, X-ray diffraction and EXAFS

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The aim of the presentation is to discuss the applicability of the titled methods in coordination chemistry, together with their theoretical basis. The examples involve complexes between organotin(IV) compounds and biologically active ligands. The ligands used for preparation contained different donor atom such as: polyhydroxy-alkyl-carboxylic acids {O,O}, captopril {O,N,S}, DNA fragments {(P)O, ribose(O)}, and picolinic acids (aromatic{N}, {O}). The bonding sites of the ligands were determined by FTIR and Raman spectroscopies. The information about the local tin environments of tin central atom were measured by using Mössbauer spectroscopy.

The EXAFS method is suitable for the determination of the local structure of organotin(IV) complexes formed both in solution or in the solid state. The method provides structural information relating to the radial distribution of atom pairs in a system: the coordination number in the first, second and sometimes in the third coordination sphere, the interatomic distances and their root mean square deviations.

X-ray crystallographic observations on compounds containing a ligand and a metal salt in stochiometric proportions do not constitute to evidence of complex formation in solution. On the basis of the crystal structures, it is not possible to predict complex formation in solution, because when the crystals are dissolved in polar solvents, hydrogen bonds may be broken and water or some other solvent molecule may displace one of the coordinated groups of the ligand from the coordination sphere of the metal ion.

A-P47

Complexation of hydronium and ammonium ions by lower rim calix[4]arene tetra(*O*-[*N*-acetyl-*R*-phenylglycine methyl ester]) derivative

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Binding of hydronium ion with 5,11,17,23-tetra-*tert*-butyl-26,28,25,27-tetrakis(O-methyl-D-α-phenylglycinecarbonylmethoxy)calix[4]arene[1] (L) in acetonitrile was studied by ^{1}H NMR spectroscopy, spectrophotometry and conductometry. NMR showed that H_3O^+ was probably bound by hydrogen bonds to the ether oxygens of calix[4]arene. The stability constant of the 1:1 complex determined at 25 °C and I_c = 0.01 mol dm^{-3} (Et_4NClO_4) by spectrophotometric titrations (lg K = 4.11) was in satisfactory agreement with the one determined by conductometry (lg K = 4.25). No significant influence of the intentionally added water upon the complexation reaction was observed up to the water volume fraction of approximately 0.05 %. The complexation of ammonium ion by L in acetonitrile was also investigated spectrophotometrically and the stability constant of the NH_4L^+ complex was found to be lg K = 2.36.

The stability of the H_3OL^+ complex is considerably lower than that of NaL^+, and the same holds for the comparison of NH_4L^+ and KL^+ complexes.[2] As in both cases the cations are of comparable size (which is important for fitting into the calix[4]arene cavity), the difference in complex stability constants is presumably due to the stronger solvation of H_3O^+ and NH_4^+ compared to Na^+ and K^+ in acetonitrile.

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A-P48

Enthalpy of transfer for the transition state of complex formation.

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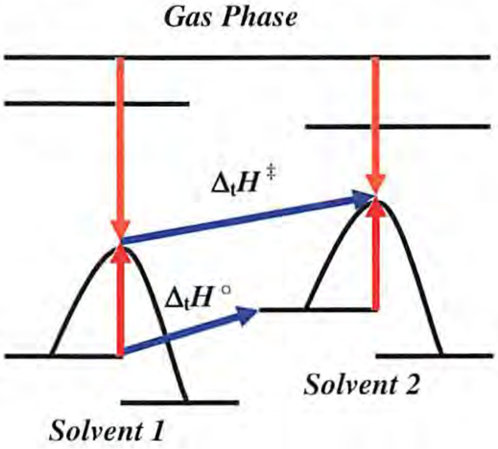
Thermodynamic and structural investigations provide us the useful information on the initial and final state of metal ion complex formation. Kinetics, however, provide that on the transition state of the complex formation. Recently, we proposed an approach of combination of thermodynamics and kinetics in order to elucidate the transition state of metal ion complexation, *i.e.*, by using the enthalpies of transfer between solvents for the transition state, $\Delta_t H^\ddagger$. It is defined as the difference of the solvation enthalpy from the transition state in gas phase to that in each solvent and easily obtained from the enthalpy of transfer for the initial state between the solvents and the activation enthalpies in both solvents. Thus, we can shed light on the solvent effect even in the transition state. Here, our recent studies on the *solvation steric effect at the transition state* will be presented.

The halogeno and/or *pseudo*-harogeno complexation in a series of amide solvents is suitable model systems for this purpose. For instance, with the first transition divalent metal ions and the lanthanoid trivalent metal ions, it is enhanced in *N,N*-dimethylacetamide (DMA) over *N,N*-dimethylformamide (DMF), despite that the electron-pair donating ability of DMA (Gutmann's donor number, D_N=27.8) is slightly higher than DMF (26.6). DMA shows a *weak solvation steric effect*, *i.e.*, an octahedral six-coordination is kept unchanged for a series of first transition metal(II) ions, except for the zinc(II) ion, although the coordination geometry around the metal ion and the intermolecular structure of DMA are significantly distorted. Odutsumi *et al* have reported that Fe(III) ion also shows a *weak solvation steric effect* in DMA. Thiocyanato complex formation of Fe(III) ion is enhanced in DMA over DMF, although Fe(III) ions has octahedrally solvated structures in both solvents. Our kinetic study in both solvents shows that Fe(III) mono-thiocyanato complex is formed *via* the associative mechanism in both DMF and DMA. Interestingly, the enthalpy of transfer for the transition state of the mono-thiocyanato complex is markedly reduced than that for the initial state, though total coordination number increases from six to seven. We will discuss in detail together with the result of the tetrachlorocobaltate(II) complex formation.



A-P49

NMR relaxation and diffusion studies of 1-butyl-3-methylimidazolium Ionic Liquids

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Since room-temperature ionic liquids (ILs) such as imidazolium and pyridinium salts have negligible vapor pressure and high chemical and thermal stabilities, they are of growing importance as a alternative to conventional organic solvents.[1] In this report, in order to understand the solvent properties of ILs, we measure the self-diffusion coefficients (*D*) and multi-nuclear (^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P) relaxation times (T_1) in [BMIM][BF$_4$] and [BMIM][PF$_6$] ([BMIM]$^+$ = 1-butyl-3-methylimidazolium cation) by NMR spectroscopy with a pulsed field gradient technique.

The temperature dependence of *D* of cationic and anionic species in [BMIM][BF$_4$] is shown in Figure 1 together with those in [EMIM][BF$_4$] ([EMIM]$^+$ = 1-ethyl-3-methylimidazolium cation).[2] Although *D* of [EMIM]$^+$ is larger than that of [BF$_4$]$^-$ in [EMIM][BF$_4$], there is no apparent difference in *D* between [BMIM]$^+$ and [BF$_4$]$^-$ in [BMIM][BF$_4$] with a longer alkyl chain. We will discuss the rotational dynamics as well as the translational diffusion in [BMIM][BF$_4$] and [BMIM][PF$_6$] in connection with the macroscopic viscosity.

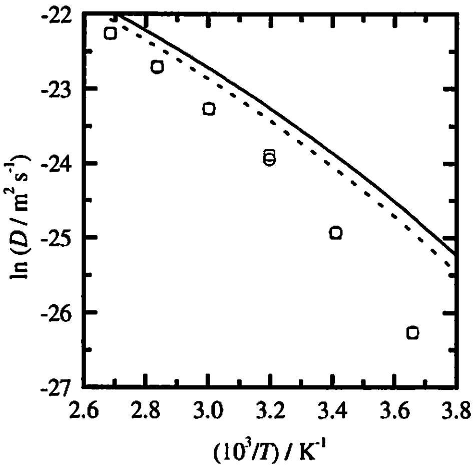

Figure 1. Arrhenius plots of *D* of cationic (circle) and anionic (square) species in [BMIM][BF$_4$]. The solid and dotted lines indicate *D* of cationic and anionic species in [EMIM][BF$_4$], respectively.

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A-P50

Radiochemical research of micro quantities of lanthanum in water solutions

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The sorption of fission fragment – ^{142}La – by phosphate titanium in water solution has been investigated by isotopic dilution analysis, using gamma spectrometry of fission fragments [1]. ^{142}La was obtained in thermal neutron induced fission of ^{235}U and was accumulated in water. To provide the reaction under study the M-10 microtron located at the Department of Nuclear Physics (Uzhgorod National University) was used. The concentration of fragment was 10^{-14} m. We've chosen such conditions of the research that radio-nuclide was, mainly, in ionic forms, and its adsorption on glass was minimized [2].

The solutions of stable La isotope, in the form of $LaCl_3{*}7H_2O$, with different concentrations were added to water with ^{142}La. The fluctuations of lanthanum concentrations were from 10^{-14} m to 10^{-3} m.

Concentrations of lanthanum of more, than 10^{-3} m, compared with the sorption of micro- and macro-quantities have been studied. In that case, the quantities of lanthanum were measured by the spectrophotometric method. The conditions of research of macro-quantities were the same as in case of micro-quantities.

The investigation shows, that lanthanum in micro-quantities is sorbed better. It is, probably, a result of its state in water solutions. Polymerization does not occur with such micro concentrations, and only ionic and hydrolysis forms of lanthanum are sorbed.

As far as other fission fragments found in solution are concerned, the conditions of the experiment were chosen in such a way that their effect on the results of investigation was minimum.

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A-P51

Kinetics and Activation Thermodynamic of Amide Bond Cleavage of α,α-Dialkylglycines Derivatives

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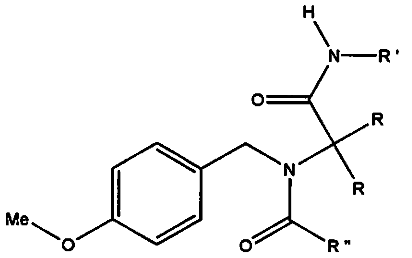
α,α-Dialkylglycines are finding applications in the synthesis of biologically important compounds. The synthesis of a series of such compounds and preliminary results of rate constants, *k*, for the cleavage of the amide bond at their C-terminus, at 25 °C were presented recently⁽¹⁾.

Having in mind to obtain an insight into the energetics of reaction, we extended the kinetic study to the dependence on temperature of *k*. The kinetics of the bond cleavage was monitored by HPLC and accurately characterised by a first-order behaviour.

According to the Transition State Theory, we obtained the activation parameters, namely, the enthalpy, $\Delta^{\neq}H$, and the entropy, $\Delta^{\neq}S$, of activation, at 25 °C



R	R'	R"	$k \times 10^4$ /s^{-1}	$\Delta^{\neq}H$/kJmol^{-1}	$\Delta^{\neq}S$/Jmol^{-1}
CH_3	C_6H_{11}	Ph	23.13	65.6	- 74.7
CH_3	C_6H_{11}	$PhCH_2$	5.07	68.8	- 76.3
CH_3	4-$CH_3OC_6H_4CH_2$	Ph	11.56	73.4	- 55.0
CH_3	4-$CH_3OC_6H_4CH_2$	$PhCH_2$	1.98	79.9	- 47.4
CH_2Ph	C_6H_{11}	Ph	3.38	60.4	- 108.3
CH_2Ph	C_6H_{11}	$PhCH_2$	2.91	65.5	- 92.4
CH_2Ph	4-$CH_3OC_6H_4CH_2$	Ph	1.96	73.4	- 69.4
CH_2Ph	4-$CH_3OC_6H_4CH_2$	$PhCH_2$	1.95	71.4	- 77.1

The role of the substituents is analysed in terms of position and size in connection with steric hindrance and conjugation effects.

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A-P52

Enthalpy of Solution of Fullerene [60] in Some Aromatic Solvents

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Fullerenes are highly symmetrical cage-like molecules of carbon, and represent a special class of spherical quasi-aromatic systems[1,2] that interact with solvent molecules in ways that provide new information on solute-solvent interactions.

Fullerene [60] has more resonance structures than fullerene [70] because of its higher symmetry[3], thus is more polarizable than C_{70} and will present larger solvation energy than C_{70} in the same solvent.

The interest in understanding the solubility of C_{60} and C_{70} arose since the solvent plays a crucial role during the extraction, isolation and purification of fullerenes. Solubility of fullerene C_{60} (and other fullerenes) in organic solvents should be influenced by several solvent properties such as the Hildebrand's solubility parameter and the polarizability.

In this work, enthalpies of solution $\Delta_{soln} H^{\theta}$ of fullerene [60] in benzene, toluene, bromobenzene, 1,2-dichrorobenzene and nitrobenzene have been measured in a Precision Solution Calorimeter at 298 K, using the ampoule breaking technique. The dissolution of C_{60} in these aromatic solvents was observed to be exothermic, with exception of benzene, in which the enthalpy is zero. We attempted to correlate ($\Delta_{soln} H^{\theta}$) of C_{60} in these solvents with the solubility; Hildebrand's solubility parameter; and polarizability parameter.

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A-P53

Excess Molar Volumes and Viscosities of Binary Mixtures of Epichlorohydrin with Alcohols at Different Temperatures

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An excess property of liquid systems, such as excess molar volume (V^E) has been a qualitative and quantitative way of providing information about molecular structure and intermolecular forces in liquid mixtures. Excess volume measurements of binary systems have been widely used to examine theories of liquid- liquid interaction in the mixtures[1-6]. Physical and thermodynamic properties, such as density and excess molar volume of binary systems have been the interest of many researchers (1-2).

Epichlorohydrin (C_3H_5ClO) has been widely employed in chemical industries (for example synthesis of epoxide resins). Very often, it is used together with other chemicals. In the study, we report the volumetric properties of binary systems of epichlorohydrin with methyl alcohol, ethyl alcohol, iso-propyl alcohol and t-butyl alcohol. Experimental data are used to obtain excess molar volume and a new correlation of this property with temperatures and mole fractions.

The densities and excess molar volumes of (epichlorohydrin + alchols) mixtures were determinated at different temperature. The graph of excess molar volumes against mole fracrtion of mixtures shows that the negative and positive slope because of charge-transfer interaction and physical forces at different temperatures, respectively.

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A-P54

Raman Spectroscopic and X-Ray Diffraction Measurements on The Solvation Structure of Halide Ions in Acetonitrile

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Anionic solvation as well as cationic solvation in electrolyte solutions is a very important phenomenon. We have investigated the solvation structure of halide ions in dimethylsulfoxide (DMSO, A_N = 19.3) and it was suggested that S atom and CH_3 groups of DMSO interact with halide ions[1]. In the present study, the solvation structure of halide ions in acetonitrile (AN, A_N = 19.3) is investigated by means of Raman spectroscopy and X-ray diffraction.

The peak due to the CH_3 symmetric stretching vibration was observed at 2944cm^{-1} in the Raman spectrum of neat AN, and around this peak, there appeared peaks due to overtones and combinations of various vibrations. Thus, deuterated acetonitrile (AN-d_3) was used in the spectroscopic study. Two shoulders appeared when NaI was dissolved in AN-d_3. One was located at the higher wavenumber side of the CN stretching band of neat AN-d_3, and the other was at the lower wavenumber side of the CD_3 symmetric stretching band.. In order to extract the main effect caused by cations, $LiClO_4$ and $NaClO_4$ were used. In the Raman spectra of these solutions, no shoulder was seen at the lower wavenumber side of the CD_3 symmetric stretching band. Chloride, bromide and iodide of tetra-n-buthylammonium (TBACl, TBABr and TBAI, respectively) were used for evaluation of anionic effect to the Raman spectra. There was no shoulder at the higher wavenumber side of the CN stretching band when TBACl, TBABr and TBAI were dissolved.

From these observations, it is concluded that the CN and CD_3 groups of AN-d_3 mainly interact with cation and anion, respectively. The peak shift of the CN stretching band toward the higher wavenumber side increased in the order $Li^+ > Na^+$ in the alkali perchlorate solutions, and that of the CD_3 symmetric stretching band toward the lower wavenumber side increased in the order $Cl^- > Br^- > I^-$ in the tetra-n-buthylammonium solutions. X-Ray diffraction measurements are being examined to determine the structure of the solvated halide ions, as well as of the cations in AN.

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A-P55

Coordinating states of metal ions in solutions of perchlorates, chlorides and bromides in dimethyl sulfoxide

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The densities and the apparent molar volumes of perchlorates, chlorides, bromides of the manganese(II) – zinc(II) series in dimethyl sulfoxide were determined. Respective partial molar volumes of salts were obtained by extrapolation technique. Using data for metal perchlorates, which exist in DMSO as the well defined hexa-solvates of $M(DMSO)_6^{2+} \cdot 2ClO_4^-$ type, the limiting partial molar volumes of the hexakis(DMSO) cations were derived and discussed in terms of the ligand field effects. The type of an anion and the electron structure of a cation effect on the partial molar volume of a salt were demonstrated and discussed. The results show that coordination states of metal chlorides and bromides in DMSO are much more complex than those of the respective metal perchlorates. Only nickel(II) bromide and cobalt(II) bromide do not form any coordinating complexes in solution at all and exist in similar form as respective metal perchlorates. Both zinc(II) bromide and zinc(II) chloride exist in DMSO solutions as the neutral tetrahedral complexes: $Zn(DMSO)_2Cl_2$ and $Zn(DMSO)_2Br_2$. Apparent molar volumes of chlorides and bromides of manganese(II) and copper(II) which are close to each other but, at the same time, differ significantly from the apparent molar volumes of their perchlorates, suggest formation of mixtures of tetra- and octahedral complexes in DMSO. The apparent molar volumes of extremally different mixtures $Zn(ClO_4)_2 - ZnCl_2$ and $Ni(ClO_4)_2 - NiBr_2$ in dimethyl sulfoxide were determined. A method, utilizing density measurements for studying solution equilibria, was suggested.

A-P56

Zeolite-supported oligomeric Cu(II) chelate complexes as pseudohomogeneous catalysts in liqui-phase oxidation

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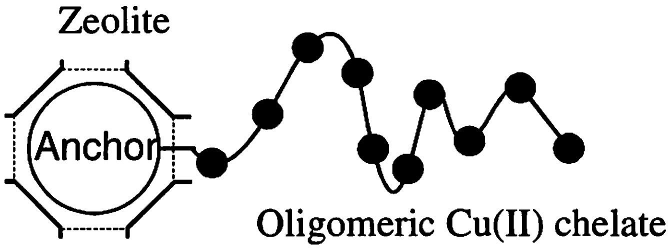
Oligomeric chelates of transition metals and polinuclear complexes are known to exhibit a prominent catalytic activity and high selectivity under mild conditions. These compounds usually are poor soluble and could not be effective homogeneous catalysts. However, after being supported the oligomeric Cu(II) chelates show the outstanding catalytic activity for liquid-phase reactions. The A zeolites are of particular interest for heterogenization of the oligomeric Cu(II) chelates.

This work reports the preparation of oligomeric Cu(II) chelates topologically anchored on molecular sieve (zeolite 5A) and the study of the catalytic behaviour in liquid-phase oxidation of 2-adamantanone with hydroxy peroxide to give corresponding lactone as a main product. The oligomeric catalyst chains were formed as shown on the scheme.



The topologically-anchored oligomeric Cu(II) chelates were proved to operate as ***pseudohomogeneous*** catalysts under conditions on consideration. The active centers of the oligomeric catalyst chains exposed to the solution are easily accessible for the substrate molecules. The catalytic activity is proportional to the amount of Cu(II) in the sample as it observed for the same reaction in the presence of the homogeneous catalyst that is monomeric Cu(II) chelate.

A-P57

Thermodynamics of solvation interactions in liquid-phase systems

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With the purpose of development of the in essence new quantitative approach for detection of functional activity of reagents in chemical processes in solutions, two approaches to investigation of a solvation under isentropic conditions (S=const) are offered. First of them takes into account of a compressibility of solvation spheres of solute ions at changing of concentration and gives rise to small temperature dependence of a molar isentropic compressibility of a solvation complex of ions and its numbers of a solvation (h). This is shown on examples of aqueous solutions of alkali metals halide, nitrate, thiosulphate and others. In this case the change of h values is the main contribution of concentration dependence of solvation process, at the same time the temperature have influence on the solvation of an electrolyte through only changing structure of a solvent. The second approach bases one-self upon more correct thermodynamic relations. The derivative of volume of a solvent on pressure at fixed S(aq) will be consisted of the derivative of solvent volume on pressure at a constancy of an entropy of a solvent (S_1^*) and the additional term (Δ_ϕ) designed from the thermodynamic equations proposed by J.C.R.Reis. The ion solvation numbers obtained can be substituted in the active mass law and enable to determine true the equilibrium constants and the rate constants (and, hence, and mechanism) of reactions in solutions. The method of precise definition of the concentration corresponding to a complete solvation ionic spheres of solute is proposed. It is based on the dependence of a rational activity coefficient of a solvent ($\gamma_R=a_w/X_1^{free}$) from hydration number of an electrolyte (h), which is typical example of a discontinuous function. The approach is realized for aqueous solutions, as well as nonaqueous solutions of electrolytes (including liquid-phase systems used in chemical powers sources).

A-P58

Title of Poster A-P58

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abstract not recieved

B-P1

Application of capillary zone electrophoresis in analysis of cephalosporins

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The cephalosporins are semisynthetic antibiotics, which are derived from the cephalosporin C (one of the fermentation products of Cephalosporium acremonium). The cephalosporin antibiotics have a β-lactam ring fused with a 6-membered dihydrothiazine ring. Since more and more cephalosporins have been found that cannot be absorbed orally and must be administrated intravenously or intramuscularly, the interest is focused on the study of the bioavailibility. Recently the capillary electrophoresis (CE) has proven to be a powerful technique for the analysis of these compounds.

For the separation of the 14 different cephalosporins investigated capillary zone electrophoresis (CZE) was used. The influence of different parameters (pH and the concentration of the buffer electrolyte, the length and the inner diameter of the capillary, applied voltage, pressure of injection) on the migration times of the cephalosporins and the efficiency of the separation were studied. The optimated method was validated by the evaluation of the selectivity, precision (migration time and peak area), accuracy, linearity and range, detection limit and quantification limit for all compounds investigated.

The method was applied also to monitor the solution stability of some selected cephalosporins in solution. The presented method seemed to be well suitable, effective tool for analysing cephalosporin antibiotics both in pharmaceutical formulations and in biological, clinical materials.

B-P2

Hydrogenation of calcium carbonate in aqueous suspension with soluble rhodium(I) catalysts

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The catalytic activation of carbon dioxide or its simple inorganic derivatives is an important field of research, both from environmental and synthetic point of view, due to the abundance of CO_2 and carbonates. Highly active catalytic systems are known for the hydrogenation of CO_2 in the presence of amines which afford formamides or ammonium formates.[1] Nevertheless, catalysts for the production of formic acid or formates in aqueous solution are still strongly needed.[2,3]

In the present work, we investigated the reaction of $CaCO_3$, CO_2 and H_2 in aqueous suspension/solutions. The reaction is catalyzed by $[RhCl(mTPPMS)_3]$ (mTPPMS = *meta*-monosulfonated triphenylphosphine) and yields calcium formate cleanly. The poster will discuss the effect of the reaction variables (pressure of CO_2 and H_2, temperature, phosphine/rhodium ratio). The most significant finding is that the final amount of formate may exceed the stoicheiometric quantity required to obtain $Ca(HCOO)_2$, i.e. free formic acid is produced.

Acknowledgement: Financial support by the Hungarian National Research Foundation (OTKA T043365) is gratefully acknowledged.

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B-P3

Metal-Glyphosate Complexation in Solution and at the Metal Oxide-Solution Interface

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Glyphosate (N-(phosphonomethyl) glycine, PMG) is a widely used herbicide due to its high activity, very low toxicity to animals and short residence time in soil. In a few days glyphosate is immobilised and degraded in the soil to the non-toxic products CO_2, PO_4^{3-} and NH_3 or adsorbed to colloidal fractions as organic matter and clay minerals. Glyphosate is strongly polar and has a zwitterion structure depending on pH. Metal ions are believed to play a role in the adsorption process of glyphosate to colloidal fractions, which makes the coordination chemistry of glyphosate very interesting.

Glyphosate (PMG) has been studied with respect to its acid-base properties and complexation with cadmium(II) and copper(II), respectively. Adsorption experiments of PMG, PMG-Cd(II) and PMG-Cu(II) complexes onto manganite (γ-MnOOH) and goethite (α-FeOOH) surfaces have been done and interpreted in terms of a surface complexation model. The model is based on data obtained from measurements with FT-IR, XPS, EXAFS[1] and potentiometric titrations.

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B-P4

Solution behaviour and catalytic properties of [RuHCl(CO)P_3]-type complexes

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Water is a polar solvent which strongly solvates ionic species. As a consequence, it may have important effects on the mechanism of reactions catalyzed by water-soluble organometallic complexes compared to the mechanism of analogous reactions in organic media. For example, in water the heterolytic splitting of H_2 to H^- and H^+ is more favoured than in non-polar organic solvents, and can even replace homolysis (e.g. by oxidative addition) with the same catalyst.[1]

We have studied the solution behaviour of [RuHCl(CO)(mTPPMS)$_3$] (mTPPMS = *meta*-monosulfonated triphenylphosphine) which had been previously used[2] as catalyst for the hydrogenation of *trans*-cinnamaldehyde. ^{1}H and ^{31}P NMR spectroscopy revealed, that in water this compound dissociated completely to yield [RuH(CO)(mTPPMS)$_3$]$^+$; however, the equilibrium was fully shifted in favour of the neutral complex in the presence of 50 equivalents of LiCl. The reaction rate and selectivity of the hydrogenations of *trans*-cinnamaldehyde was strongly effected by the presence of chloride, presumably through this equilibrium. Although [RuH(CO)(CH_3CN)(PPh_3)$_3$]$^+$ is a known compound,[3] such an effect on the catalytic properties has not been reported.

Acknowledgement: Financial support by the Hungarian National Research Foundation (OTKA T043365) is gratefully acknowledged.

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B-P5

The effect of dissolved oxygen in aqueous solution for the TiO_2 photocatalysis and the role of adsorbed Ln ion on the TiO_2 surface

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In the photocatalysis of titanium dioxide(TiO_2), water molecules need to exist on the TiO_2 surface because the generated electrons from the TiO_2 surface by the UV irradiation react with the adsorbed water on the surface and the active species are produced. Therefore, it is important for the acceleration of this reaction to increase the amount of adsorbed water on the TiO_2 surface. And also, the oxygen dissolving into aqueous solution(dissolved oxygen) enormously play important role in this reaction(1). This study aims to confirm the effect of the dissolved oxygen for the decomposition function of TiO_2 and to further increase the amount of adsorbed water. To develop the applied investigation, we selected Lanthanide ions(Ln=Ce, Sm, Eu, Yb) for the adsorbed metal ions. Because Ln ions readily form the coordination bond with H_2O molecules in aqueous solution. We prepared some Ln/TiO_2 photocatalyst powders adsorbing Ln ions on the TiO_2 surfaces to employ this feature. We employed 2-propanol for the reaction solution and evaluated the photocatalytic level by means of ^{1}H-NMR. The Ln/TiO_2 structure in dry powder was analyzed by means of EXAFS(2). These results showed the characteristic role of Ln ions. This paper will report the role of Ln ions and the importance of adsorbed water for photocatalytic reaction which is evaluated from the effect of dissolved oxygen.

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C-P1

Potential Insulin-Mimetic Complexes with a $Zn(O)_4$ coordination mode: synthesis, speciation and toxicity in rat isolated hepatocytes

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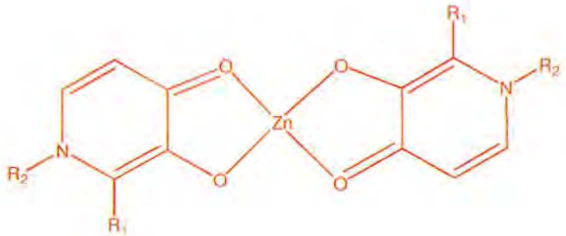
Zinc is an essential element for man as it plays a role in a number of healing processes and the beneficial therapeutic effects of zinc compounds have been recognized, namely that Zn(II) salts act as insulinmimics.[1] More recently it has been reported that a $Zn(O)_4$ coordination mode is advantageous, in what concerns the inhibition of free fatty acids, when compared with zinc and vanadyl sulphates.[2]

In this work we report the synthetic procedure and characterization of zinc(II) complexes with 3-hydroxy-4-pyridinones which have been obtained as hydrates. Stability constants have been determined and speciation diagrams as a function of pH and metal:ligand ratio have been established in water by potentiometric methods. Toxicity of the complexes is being evaluated in rat isolated hepatocytes and compared with zinc salts and vanadium parent compounds.



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C-P2

Speciation in the (Peroxo)vanadate - Picolinate System

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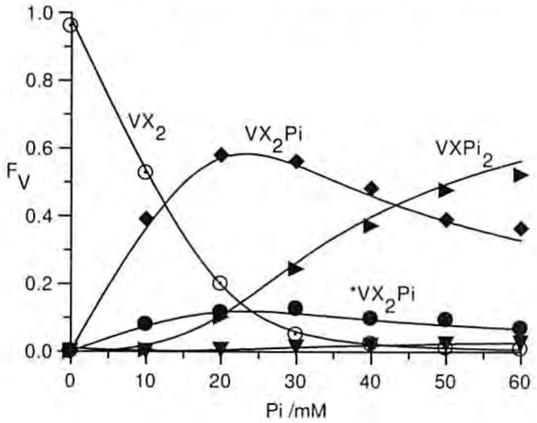
Peroxovanadates have recently received wide attention due to their biochemical significance, most notably insulin-mimetic behaviour. It is vital to know the complete speciation in vanadate systems containing different ligands e.g. picolinate (Pi). A potentiometric (glass electrode) and ^{51}V NMR (Bruker AMX-500 MHz) spectroscopic investigation of the systems has been performed at 25 °C in 0.15 M Na(Cl). The medium was chosen to represent physiological conditions. The computer program LAKE [1], designed to simultaneously treat multimethod data, was used to establish the speciation. Before studying the $H^+ - H_2VO_4^- -$ Pi and $H^+ - H_2VO_4^- - H_2O_2 -$ Pi systems, the complete speciation in the subsystems $H^+ - H_2VO_4^-$ and $H^+ - H_2VO_4^- - H_2O_2$ must be known under the same experimental conditions [2].

In the ternary $H^+ - H_2VO_4^- -$ Pi system, six species were found. The major acidic species VPi (-536 ppm), changes chemical shift upon deprotonation to a minor VPi^- (-550 ppm) species, and its resonance sharpens. At pH > 3, the dominating species are the tree isomers VPi_2^- (-513 ppm), $*VPi_2^-$ (-530 ppm) and $**VPi_2^-$ (-553 ppm). Asterisks denote minor species.

In the quaternary system, seven new ^{51}V resonances were observed. Five of these are in the downfield VX region and the corresponding complexes are VXPi (-600 ppm), $*VXPi^-$ /$*VXPi^{2-}$ (-658 ppm), $VXPi_2^-$ (-632 ppm), $*VXPi_2^-$ (-611 ppm) and $**VXPi_2^-$ (-616 ppm), where X denotes the peroxo ligand. The other two resonances are in the upfield VX_2 moiety region and originate from the complexes VX_2Pi^{2-} (-745 ppm) and $*VX_2Pi^{2-}$ (-741 ppm). Complexation is very strong and equilibrium is attained within 15 minutes. The decomposition of hydrogen peroxide is marginal even in acidic solutions, enabling the to investigation of the system over the wide pH range 1.5 - 10.

The figure shows the distribution of vanadium, F_V, as a function of c(Pi) at c(V) = 20, $c(H_2O_2)$ = 40 mM and pH ~ 5.5. The symbols represent experimental NMR points and the fit to the calculated curves model is very good. Formation constants will be given for all species.



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C-P3

Impact of Z- E- isomerism and number of Δ-aminoacid residues on binding abilities of dehydropeptides.

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Dehydropeptides are natural or synthetic peptides that include double bond between α- and β-carbons in amino acids side-chains. They have interesting biological and chemical properties. The most known biological activity of dehydropeptides is antibiotic activity[1]. Some dehydropeptides are derivatives of natural peptides [*e.g.* hormones[2]]. It is interesting that insertion of (Z) or (E) isomers of dehydroamino acids into the peptide molecule influence distinctly its biological activity. The Z-isomers are more common and they are foud, e.g. in antibiotics.

Presence of double bond between α- and β-carbons have a strong impact on coordination ability of dehydropeptides. They are more effective ligand for metal ions than adequate peptides without dehydroamino acids[3]. The two major effects influence the binding of metal ions to dehydropeptides. One derives from the electronic properties of the $C_\alpha = C_\beta$ double bond, second one from the steric features of dehydropeptides[4]. The study on the binding ability of Z-, E-dehydropeptides shown, that the Z-isomers are more effective ligands for metal ions *e.g.* Cu(II), Ni(II), than E-isomers. The presence of bulky side chain in the dehydroamino acid residue may also be critical for the coordination mode.

Acknowledgements:
This study was supportedb by grant No. 441, of the Wrocław Medical University

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C-P4

Investigation of solution equlibiria between alumnium (III)-ion and L-histidine by ^{27}Al , ^{13}C and ^{1}H –NMR spectroscopy

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Solution equilibria between aluminium (III)-ion and L-histidine at Al to His concentration ratio 1:5 (C_{Al} =50 mM; C_{his} = 250mM) and pH values between 1.8 and 6.4 have been studied by ^{27}Al, ^{13}C and ^{1}H –NMR spectroscopy. Some of obtained ^{27}Al –NMR spectra are shown in Fig1.

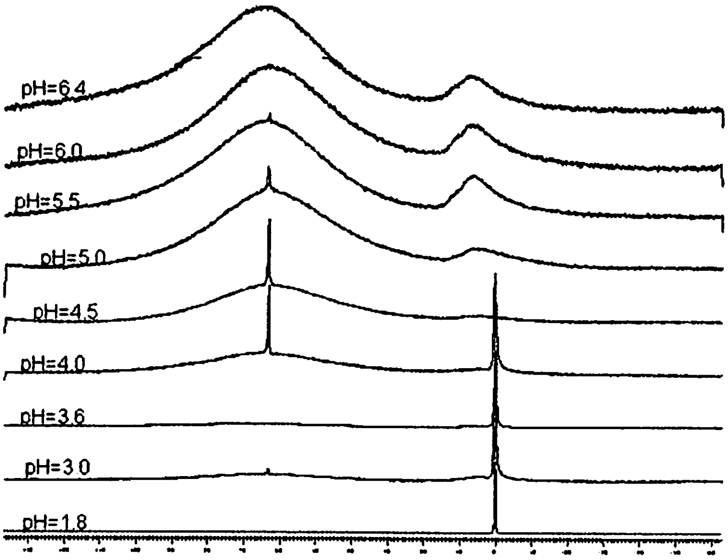

Fig.1. ^{27}**Al –NMR spectra of Al+His solutions**

The obtained results show that complex formation between Al^{3+} and L-histidine begins at pH=5.0 and concentration ratio [His] to [Al] 1:5
Upon rising the pH from 4.5 to 6.4 Al^{3+} signal at δ=0 dissappears and new medium –broad signal appears which is slightlly shifted downfield.

In the same time signal arising from tridecamer at δ=66 ppm dissappears at pH ≈5.5 showing that at this pH value $Al(OH)_4^-$ dominates .It may be calculated that the dominating Al-His complex in solution may have the composition $Al(OH)(Hhis)^{2+}$ and further work on confirmation of this in in progress.

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C-P5

Metal Ion Complexes of 5- and 6-Uracilmethylphosphonate ($5Umpa^{2-}$ and $6Umpa^{2-}$) in Aqueous Solution

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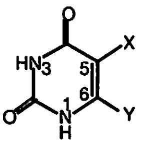
Derivatives of 5- and 6-uracilmethylphosphonate prolong in combination with *Cisplatin* the survival time of mice with lymphoid leukemia.[1] Since metal ions are likely to be involved in the biological action of these phosphonate derivatives, we extended our earlier studies[2] of the Mg^{2+} and Ca^{2+} complexes of $5Umpa^{2-}$ and $6Umpa^{2-}$ by determining the stability constants of the complexes with Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} (= M^{2+}) in aqueous solution (potentiometric pH titrations; 25 °C; I = 0.1 M, $NaNO_3$). By using previously established straight-line plots of $\log K^{M}_{M(R\text{-}PO_3)}$ *versus* $pK^{H}_{H(R\text{-}PO_3)}$ (where $R\text{-}PO_3^{2-}$ = simple phosphate monoester or phosphonate ligands with a non-interacting residue R), it is shown that the M(6Umpa) complexes have the stability expected on the basis of the basicity of the phosphonate group in $6Umpa^{2-}$; i. e., this ligand may be considered as a simple analogue of uridine 5'-monophosphate, whereas the M(5Umpa) complexes are slightly more stable by about 0.1 to 0.3 log units, which is indicative of a M^{2+} nucleobase interaction.



$5Umpa^{2-}$: $X = -CH_2PO_3^{2-}$
$Y = -H$
$6Umpa^{2-}$: $X = -H$
$Y = -CH_2PO_3^{2-}$

In the higher pH range deprotonation of the uracil residue occurs with formation of $M(5Umpa\text{–}H)^-$ and $M(6Umpa\text{–}H)^-$ complexes. By taking into account recent results[3] for complexes of M^{2+} with N3-deprotonated uridine preliminary evaluations show that a second M^{2+} can be coordinated to the deprotonated uracil moiety in the $M(5Umpa\text{–}H)^-$ and $M(6Umpa\text{–}H)^-$ species with formation of binuclear $M_2(5Umpa\text{–}H)^+$ and $M_2(6Umpa\text{–}H)^+$ complexes. A discussion of the stabilities and structures of the complexes will be presented.

Supported by the Swiss National Science Foundation, the Swiss Federal Office for Education & Science (COST D20), and the Medical University of Łódź.

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C-P6

Phosphine-substituted water-soluble (arene)Ru(II)-complexes

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(η^6-Arene)ruthenium(II)-complexes have been subject to intensive studies for many years due to their interesting coordination chemistry and catalytic properties.[1] Their use as catalysts in aqueous and biphasic systems[2] may allow practical realization of important processes such as the hydrogenation of arenes.[3] In the present work, we have found that the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with hydrogen in the presence of the water-soluble phosphines mTPPTS (*meta*-trisulfonated triphenylphosphine) and PTA (1,3,5-triaza-7-phosphaadamantane) afforded as the main species $[(\eta^6\text{-}C_6H_6)RuH(TPPTS)_2]^+$ **1**, $[(\eta^6\text{-}C_6H_6)RuH(PTA)_2]^+$ **2**, $[(\eta^6\text{-}p\text{-cymene})RuH(TPPTS)_2]^+$ **3**, and $[(\eta^6\text{-}p\text{-cymene})RuH(PTA)_2]^+$ **4**. Prolonged hydrogenation at elevated temperatures led to the formation of the arene-free $[RuH(PTA)_4X]$ ($X = Cl^-$ or H_2O), $[RuH_2(PTA)_4]$ and $[RuH(PTA)_5]^+$ complexes. Compounds **1-4** catalyze the hydrogenation of bicarbonate to formate in aqueous solutions at $p(H_2) = 100$ bar, $T = 50\text{-}70$ °C.

Acknowledgement: Financial support was provided by the Hungarian National Research Foundation (OTKA T043365) and by the Swiss National Science Foundation (2000-067976.02).

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C-P7

TRANSMISSION OF MAGNETIC INTERACTIONS BY ORGANOMETALLIC COUPLERS. METALLOCENE SUBSTITUTED NITRONYL-NITROXIDE RADICALS.

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Synthesis of metallocene-nitronyl-nitroxide compounds of the iron triade by condensation of metallocene -mono-, di- and tri-aldehydes with hydroxylamines and oxidation is reported. This rare organometallic derivatives with one, two and three nitronyl-nitroxide free radicals show interesting electronic interaction through the central metal. Here we report on the synthesis, epr spectroscopy, magnetic susceptibility measurements and structures of the mono- and diradical- ferrocene and triradical- ruthenocene compounds.

Reaction of the diradicals and triradicals with manganese hexafluoracetylacetonate gives, depending on the reaction conditions different magnetic clusters with two- or three-dimensional extended structures.

Angew. Chemie, 2000, *112* , 3842
Chem.Commun., 2002, 2343

We are grateful for genereous support by the Fonds zur Förderung der Wissenschaftlichen Forschung, Vienna (Project P13128), the Austrian Federal Ministry of Science (BMWV), the Accion Integrada Hispano-Austriaca HU 1999-0015 and the Human Capital and Mobility Program of EU (Network: ERB CHRXCT 940538).

C-P8

Binding Constant of VO(IV) to Transferrin

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Since the discovery of the insulin mimetic effect of vanadium, extensive research works have been made not only to prepare and test more and more new complexes, but also to monitor their possible transformations and to determine their actual chemical forms during their transport in the blood stream and to the target muscle and fat cells, where they exert the physiological actions. The speciations of VO(IV) were determined with the low molecular mass components of the blood serum (e.g. citrate, lactate, phosphate, oxalate) in the case of several carrier ligand. In this work we focus to the oxovanadium(IV) binding of the high molecular mass components of the blood serum: transferrin (TF) and albumin (HSA). The results in this field are contradictory. Namely, Chasteen et al. [1] reported K(VO-TF)/K(VO-HSA) ~ 6 which means that the HSA should be the main VO(IV) binder as $c_{HSA}/c_{TF} \sim 11$ in the serum, while ion-exchange chromatography measurements [2] suggested the predominance of the transferrin bound vanadium in the serum. Here we report our recent results obtained for the ligand competition reactions of VO(IV) between transferrin and 1,2-dimethyl-3-hydroxy-4(*1H*)-pyridinone or nitrilotriacetic acid in order to determined their binding constants. Detailed UV- room temperature and frozen solution EPR spectroscopic measurements suggest $\log K_{cond.}$(VO-TF) = 14.3 ± 0.6 (pH=7,5, $c_{HCO_3^-} = 0{,}025$ M).

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C-P9

Synthesis and spectroscopic characterisation of guanfacine with transitional metals.

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Guanfacine (N-amidino-2-2,6,dichlorophenyl acetamide hydrochloride), a centrally acting antihypertension drug, is used to treat high blood pressure. It also stimulates planning and working memory of humans. The efficiency of that kind of drugs is improved when they act in the form of their metal complexes. In this paper we report the synthessis of a series of transitions metal complexes: $[Cu(GUAF)_2](C_6H_5COO)_2$, $[Cd(GUAF)_2](C_6H_5COO)_2$, $[Cd(GUAF)_2][HgL_4]$, $[MnGUAF)_2][HgL_4]$. The given formula was confirmed by elemental analysis. Structural studies including UV-VIS, FT-IR, FT-Raman and EPR spectroscopy were performed in order to establish the conformational and structural changes appearing on complexation. Comparison of the FT-IR and FT-Raman spectra of the ligands and the corresponding complexes allowed us to predict the coordination geometry. The complexes appear to be tetragonally coordinated and the metal to ligand molar ratio is found to be 1:2 for all compounds.

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C-P10

Synthesis, vibrational and EPR analysis of new complexes of pyrazinamide with transitions metal (II)

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Four new mixed complexes combinations of pyrazinamide (pyrazinecarboxamide) have been prepared and analysed by UV-VIS, FT-IR, FT-Raman and EPR spectroscopy: $[Me(PZA)_nX_m]$, where Me = Cu^{II}, Cd^{II}, Ni^{II}, Mn^{II} and X = $[Hg(SCN)_4]^{2-}$.

Pyrazinamide (PZA) is a well known anti-tubercle bacillus drug. The spectral features suggest that the compounds are similar in structure to the Hofmann-type complexes formed with $[Hg(SCN)_4]^{2-}$ anions bridged by $[Me(PZA)]_2^{2+}$ cations. PZA can coordinate through the pyrazine ring nitrogens, the >C=O and/or $-NH_2$ groups. FT-IR and FT-Raman techniques are diagnostic of the coordination mode of PZA in complexes. The given formula was confirmed by elemental analysis and the ligand to metal molar ratio is found to be 2:1 for Cd^{II} containing complexes and 1:1 in the case of Cu^{II}, Ni^{II}, Mn^{II}.

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C-P11

Phosphine-substituted water-soluble (arene)Ru(II)-complexes

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(η^6-Arene)ruthenium(II)-complexes have been subject to intensive studies for many years due to their interesting coordination chemistry and catalytic properties.[1] Their use as catalysts in aqueous and biphasic systems[2] may allow practical realization of important processes such as the hydrogenation of arenes.[3] In the present work, we have found that the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with hydrogen in the presence of the water-soluble phosphines mTPPTS (*meta*-trisulfonated triphenylphosphine) and PTA (1,3,5-triaza-7-phosphaadamantane) afforded as the main species $[(\eta^6\text{-}C_6H_6)RuH(TPPTS)_2]^+$ **1**, $[(\eta^6\text{-}C_6H_6)RuH(PTA)_2]^+$ **2**, $[(\eta^6\text{-}p\text{-cymene})RuH(TPPTS)_2]^+$ **3**, and $[(\eta^6\text{-}p\text{-cymene})RuH(PTA)_2]^+$ **4**. Prolonged hydrogenation at elevated temperatures led to the formation of the arene-free $[RuH(PTA)_4X]$ ($X = Cl^-$ or H_2O), $[RuH_2(PTA)_4]$ and $[RuH(PTA)_5]^+$ complexes. Compounds **1-4** catalyze the hydrogenation of bicarbonate to formate in aqueous solutions at $p(H_2) = 100$ bar, T = 50-70 °C.

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C-P12

Complex formation of Salicylglycine with Ca(II), Mg(II) and Al(III)

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The active site of a metalloenzyme usually consists of several donor atoms or groups in a special arrangement to be able to bind metal ions. The metal centre formed is responsible for the activity of the enzyme. In order to understand the role of the metal ions in mechanism of enzymes and developing new synthetic metalloenzymes, it is necessary to know more about the interaction of metal ions with peptides and proteins. For modelling the interactions of proteins/peptides with hard metal ions the complex formation of salicylglycine (SalGly) with Ca(II), Mg(II) and Al(III) ions was studied in aqueous solution using pH-potentiometric, UV-vis spectroscopic techniques and dynamic light scattering measurements. Al(III) ion was found to form more stable complexes with SalGly than Ca(II) or Mg(II) ions. While Al(III) ion forms various 1:1 complexes of different protonation states in the pH range 2–7. Ca(II), Mg(II) ions seem to interact with SalGly only in the basic pH range and form mixed hydroxo species MLH_{-1} at pH > 8. According to the UV-vis spectroscopic measurements in the species MLH_{-1} the carboxylate-O^- atom and the phenolate-O^- coordinate to the metal ions. In the species $AlLH_{-2}$, formed at pH > 5.5, besides the direct coordination through the COO^- donor the phenolic-OH is assumed to be in hydrogen bonding with the metastable hydrolytic product of Al(III). Deprotonation of the peptide amide NH does not occur in these systems.

C-P13

Binding and decomposition of GSNO by Ni(II). Comparison with other metal ions.

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S-nitroso-glutathione (GSNO) and other low molecular weigh S-nitrosothiols (RSNO) play not only a crucial role in transport processes of nitric oxide (NO) but they are also important regulators of several protein functions [1]. Their physiological role concerning NO transport requires high stability to carry nitic oxide but on the other hand not high enough, to be able to release the load inside the cell. It is also known that some metal ions, especially transition ones cause accelerated decay of GSNO to GSSG and NO [2]. We hereby present a wide spectrum of stability studies of chosen S-nitrosothiols *in vitro*, indicating unusually important influence of gamma-residue of glutamic acid on the stability of the most important S-nitrosothiol: GSNO. Moreover, we show the influence of some Crucial metal ions (Cu(II), Ni(II), Zn(II) and Cd(II)) on the stability of these compounds along with the results of complexation studies revealing the thermodynamic properties of the species formed in solution.

Acknowledgment:

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C-P14

Specific behaviour of prion octarepeat domain in binding of copper(II) ions

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Transition metal ions such as copper, iron and manganese are known to be widely involved in the oxidative and inflammatory events occurring in aging and in neurodegenerative disorders, including Parkinson's disease, Alzheimer's disease and FALS.[1] Prion based diseases share with the disorders mentioned above many pathologic features, including an oxidative damage of the brain and accumulation of the aggregated proteins. The N-terminal part of the PrP apoprotein containing the fragment 29-124 is unstructured.[2] Residues 51-91 contain an unusual glycine-rich repeat every eight residues. PrP was shown to selectively bind copper within the octarepeats (PHGGGWGQ) region.[3] The solution and solid state studies have shown that at around pH 7.4 the Cu(II) complex with metal ion coordinated to imidazole and two Gly amide nitrogen atoms dominates, both in solution[4,5] and the solid state.[5] Substitution of three Gly residues with other amino acids leads to destabilization of biologically relevant Cu^{2+} complex.[6]

The complete repeat domain, consisting of four following octapeptides PHGGGWGQ that follow the nonapeptide of sequence PQGGGGWGQ, is believed to bind up to five Cu(II) ions cooperatively, with increasing affinity.[7] To test this hypothesis we have studied Cu(II) ion binding by peptide systems that mimics respectively dimmer and tetramer of octarepeat by means of potentiometric titrations and spectroscopic techniques (UV-VIS, CD, EPR and NMR).

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C-P15

Biomimetic Activation of Dioxygen by Dioximatoiron(II) Complexes

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The iron(II) complexes [Fe(Hdmed)$^+$], [Fe(Hdmpd)$^+$] and [Fe(Hdmdt)$^+$] of the dioximato ligands $R[N{=}C(CH_3)C(CH_3){=}NOH]_2$ have been synthesized, where R is CH_2CH_2, $CH_2CH_2CH_2$, and $CH_2CH_2NHCH_2CH_2$, respectively. The new complexes have been structurally characterized by X-ray diffraction, Mössbauer Spectroscopy, Electrospray Ionization Mass Spectroscopy and by comparison with analogous complexes of other transition metal ions.

Similarly to the ferroxime(II) complexes[1], the new iron(II) complexes exhibit catalytic activity in the catecholase type biomimetic oxidation of 3,5-di-*tert*-butylcatechol (H_2dtbc) with dioxygen. Detailed kinetic studies of the catalytic oxidation have been carried out by gas volumetric and spectrophotometric techniques. The observed kinetic behavior is consistent with a mechanism involving the formation of a ternary catalyst-substrate-dioxygen complex as active intermediate, followed by intramolecular electron transfer to afford a semiquinone anion radical, which is then rapidly oxidized to the corresponding *o*-quinone. The reaction is accelerated by added base (triethylamine, proton sponge), promoting coordination of the substrate to the catalyst.

Acknowledgment. This work was supported by the Hungarian Science Fund (OTKA Grant T 29036).

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C-P16

A two-dimensional EPR study of copper(II) and some N-substituted bis(aminomethyl)phosphinic acids. Microspeciation and coordination modes

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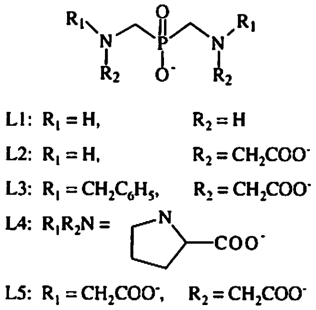
Copper(II) complexes of five substituted aminophosphinic acids were studied in aqueous solution. The EPR spectrum packages recorded at various metal-to-ligand concentration ratios and pH were analysed by the "two-dimensional" computer simulation method[1] which results in the formation constants and the EPR parameters of the various (micro)species simultaneously. We have found that the coordination of the phosphinate-O occurs in protonated complexes of L1. For ligands L2, L3 and L4, the coordination in different protonation states is reminiscent of *mono* and *bis* complexes of simple amino acids. Here, however, the *cis* positions of the amino groups in CuL are ensured by the structure of the ligand, and the isomers differ from each other in the (equatorial or axial) position of the second carboxylate group. For L3 and L4, the dimerization of this species has been shown. For L3, L4 and L5, the complex CuLH, and for L4 and L5, the species $CuLH_2$ as well, have been identified. For L5, the dimerization of CuLH and CuL predominates.



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C-P17

TERNARY COMPLEXES of PALLADIUM(II) with THIOETHER and IMIDAZOLE LIGANDS

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Sulfur containing ligands are generally considered as the primary ligating sites and transporting agents of platinum anticancer drugs under physiological conditions. The thermodynamic equilibrium of multicomponent systems and the biological activity of platinum complexes are, however, connected to the metal ion coordination of the nitrogen donor ligands including guanine and/or imidazole. Ternary palladium(II) complexes are frequently used models to mimic the binding properties of the various platinum containing drugs.

The solution equilibria, formation kinetics and structure of the ternary complexes formed in the reaction of monofunctional palladium(II) species ($[Pd(dien)]^{2+}$, $[Pd(terpy)]^{2+}$, $[Pd(bpma)]^{2+}$ and $[Pd(dipeptideH_{-1})]$) with monodentate thioether (Ac-Met) and imidazole (Ac-His, Ac-Hm) ligands were studied by potentiometric, stopped flow and ^1H NMR measurements [1-3]. It was found that the coordination of imidazole-N donor atoms results in the highest thermodynamic stability of ternary complexes, while the thioether complexes were characterised by much faster formation kinetics. On the other hand, both kinetic and thermodynamic parameters of thioether complexes were very much influenced by the other donor functions present in the binary palladium(II) complexes. The following stability order was obtained for the coordination of Ac-Met: $[Pd(dien)]^{2+} > [Pd(GlyGlyH_{-1})] > [Pd(terpy)]^{2+} \sim [Pd(bpma)]^{2+} > [Pd(GlyMetH_{-1})]$, while the rate of substitution reactions was the highest for $[Pd(terpy)]^{2+}$ and $[Pd(bpma)]^{2+}$.

The metal ion coordination of imidazole nitrogen donors resulted in the formation of mono- and dinuclear complexes containing N(1) or N(3) and both donor sites, respectively. The linkage isomers of the mononuclear complexes were identified by NMR spectroscopy and it was found that the ratio of isomers is a very sensitive function of the steric and electronic effects caused by the tridentate ligands.

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This work was supported by the Hungarian Scientific Research Fund (*OTKA T034361* and *OTKA TS040685*).

C-P18

SYNTHESIS AND COMPLEXATION PROPERTIES OF THE N,N',N'-TRIS(CARBOXYMETHYL-AMINOMETHYL)-PHOSPHINIC ACID

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In the last decades there is an increasing interest in the lanthanide(III) complexes of the open-chain and macrocyclic polyaza-polycarboxylates, polyphosphonates and phosphinates because of their successful use in medical diagnosis and therapy. Therefore it is essential to "design" new ligands and also to examine their equilibrium and kinetic properties.

Recently we are interested in the synthesis and complexation study of the polyaza-polycarboxylates containing an in-chain phosphinate group, because phosphinic acid peptides are specific inhibitors of peptide hydrolytic enzymes since the nonhydrolyzable –P(O)OH-CH_2 bond resembles the transition state of the hydrolyzable peptides.

Some symmetric derivatives of the bis(N-methyl)phosphinic acid, the bis-(glicinato-aminomethyl)phosphinic acid (H_3bgmp) and the bis(iminodiacetic-aminomethyl) phosphinic acid (H_5bimp) were synthesized and studied in our laboratory earlier. Now we have prepared an asymmetric derivative, the N,N',N'-tris(carboxymethyl-aminomethyl)phosphinic acid (H_4tcap).

We found a new procedure for the synthesis of the ligand H_4tcap with the use of the Mannich-type reaction.

The stability constants of the complexes formed with the ligand tcap have been determined by pH-potentiometric titration. The equilibrium model was also supported spectrophotometrically. The kinetic stability of the complexes was found to be relatively low. The metal-exchange reactions of the complexes could be studied by stopped-flow method.

C-P19

The effect of dissolved oxygen in aqueous solution for the TiO_2 photocatalysis and the role of adsorbed Ln ion on the TiO_2 surface

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In the photocatalysis of titanium dioxide(TiO_2), water molecules need to exist on the TiO_2 surface because the generated electrons from the TiO_2 surface by the UV irradiation react with the adsorbed water on the surface and the active species are produced. Therefore, it is important for the acceleration of this reaction to increase the amount of adsorbed water on the TiO_2 surface. And also, the oxygen dissolving into aqueous solution(dissolved oxygen) enormously play important role in this reaction(1). This study aims to confirm the effect of the dissolved oxygen for the decomposition function of TiO_2 and to further increase the amount of adsorbed water. To develop the applied investigation, we selected Lanthanide ions(Ln=Ce, Sm, Eu, Yb) for the adsorbed metal ions. Because Ln ions readily form the coordination bond with H_2O molecules in aqueous solution. We prepared some Ln/TiO_2 photocatalyst powders adsorbing Ln ions on the TiO_2 surfaces to employ this feature. We employed 2-propanol for the reaction solution and evaluated the photocatalytic level by means of ^{1}H-NMR. The Ln/TiO_2 structure in dry powder was analyzed by means of EXAFS(2). These results showed the characteristic role of Ln ions. This paper will report the role of Ln ions and the importance of adsorbed water for photocatalytic reaction which is evaluated from the effect of dissolved oxygen.

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C-P20

RNA hydrolysis in the presence of copper(II) complexes of aminoglycoside antibiotics

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The solution study on copper(II) coordination properties of aminoglycosides by means of potentiometry, UV-Vis, circular dichroism, EPR and cyclic voltammetry exhibited strong affinity of these antibiotics towards Cu(II) ions [1-3]. They anchor cupric ions by {NH_2, O^-} chelates of both aminosugar rings of their molecules. Cyclic voltammetry investigations, kinetic studies of H_2O_2 disproportionation and ROS detection experiments, allowed to further support the mechanism of oxidative reactivity of cupric complexes of aminoglycosides, which involves Cu(I) and Cu(III) redox states and both metal-bound and free ROS [3]. We also found that the complexes react with oxidation-susceptible biomolecules: 2'-deoxyguanosine, plasmid DNA and yeast $tRNA^{Phe}$ in both presence and absence of hydrogen peroxide [4, 5].

Hereby we present the results of the tRNA hydrolysis experiments. The cleavage efficiency was dependent on the resultant charge of the molecule. A comparative assay using $tRNA^{Phe}$ devoid of the natural hypermodification in the anticodon loop proved that hypermodification is indispensable for site recognition and subsequent cleavage [6]. Some of these reactions may play a role in toxic effects of aminoglycoside antibiotics.

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C-P21

Synthesis, structure and reactivity of hydroxyimino Schiff's base complexes of manganese(II)

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Similarly to our earlier work on iron(II) complexes with catecholase activity, we have recently synthesized new manganese(II) complexes using ligands H_2L of the general formula $R[N{=}C(CH_3)C(CH_3){=}NOH]_2$, where $R=CH_2CH_2$ (**1**), $CH_2CH_2CH_2$ (**2**), $CH_2CH_2NHCH_2CH_2$ (**3**). The following reaction was used to prepare derivative **3** as the tetraphenylborate salt:

$$2MnCl_2 + 2H_2L + 2NaB(C_6H_5)_4 \rightarrow [Mn(HL)]_2[B(C_6H_5)_4]_2 + 2HCl + 2NaCl$$

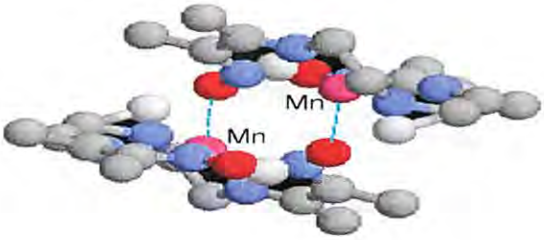

Figure 1

These new complexes were characterized by IR-spectroscopy, ESI-MS and X-ray diffraction. These studies revealed that the complexes have a dimeric structure. Figure 1 shows the structure of the dimeric manganese(II) complex $[Mn(HL)]_2^{2+}$ in the case of derivative **3** without the $B(C_6H_5)_4^-$ counter-ions. The two near-planar halves of the molecule are held together by Mn-O-N bridges formed by the oximato groups. Studies on the catalytic activity in the oxidation of substituted catechol derivatives are in progress.

Acknowledgement: This work was supported by the Hungarian Research Fund
(OTKA Grant T34282).

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C-P22

THE EFFECT OF CARBOXYLATE GROUP ON THE COMPLEXATION OF AMINO ACID DERIVATIVES OF BIS(IMIDAZOL-2-YL) GROUP

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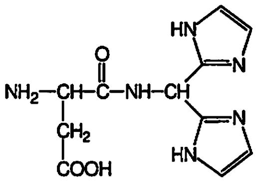
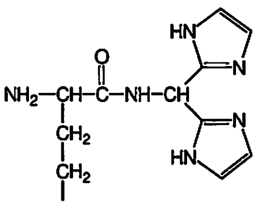
The ligands containing chelating bis(imidazol-2-yl) groups can potentially mimic the active site of metalloenzymes, in which two or more imidazole and/or negatively charged imidazolato groups bind the metal ions. The two imidazole nitrogens of bis(imidazol-2-yl) group forming a six membered chelate are stable binding sites for metal ions studied (Cu(II), Ni(II), Zn(II)). The potential donor atoms of the amino acid chain connected to the bis(imidazol-2-yl) groups are, however, able to change this coordination mode, if the ligand has free terminal amino group in chelatable position with the amide and imidazole nitrogens.

The carboxylate group in the side chain of amino acid has effect on the complexation of ligands. The results of the copper(II) and nickel(II) complexes of four amino acid derivatives containing bis(imidazol-2-yl) group (Figure) will be presented.



α-Asp-BIMA



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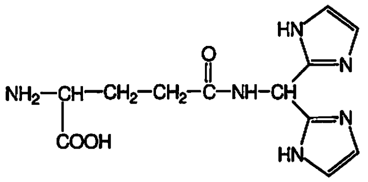
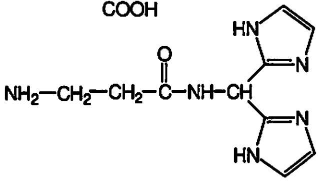


γ-Glu-BIMA



β-Ala-BIMA

Acknowledgement: The work was supported by the Hungarian Scientific Research Fund (OTKA TS040685 and T042722).

C-P23

High performance chromatographic (HPLC) method for identification of captopril in solution - the effect of pH

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Stability of captopril in aqueous solution depends on a series of factors like temperature, light, humidity and pH.

Captopril was dissolved in 0.1 N NaOH solution and we have examined the influence of pH on the identification of captopril by HPLC.

Aqueous solutions of captopril at different pH values (pH= 2, 4, 6, 8, 10) have been chromatographed at the following time intervals t_0, $t_{\text{one week}}$, $t_{\text{two week}}$, $t_{\text{one month}}$, $t_{\text{two months}}$. These tests showed quite well that captopril is stable under acidic conditions. Therefore, for future HPLC measurements of captopril acidic aqueous sample solutions should be used for good reproducibility.

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E-P1

Hydration structure of magnesium(II) ion at high temperatures and high pressures

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The structure of hydrated magnesium(II) ion is a six-coordinated octahedron in water at room temperature and atmospheric pressure. The change of hydration structure of magnesium(II) ion has been studied with increasing temperatures and pressures.

The Raman spectra of magnesium(II) chloride aqueous solutions with varying concentrations were measured at 25 °C and 0.1 MPa. The intensity of the Raman band due to the O-H stretching vibration of hydrogen bonded water molecules decreased and that of water molecules bound to ions increased with increasing magnesium(II) chloride concentrations. Hydrogen bonded water structure was broken with increasing magnesium(II) chloride concentrations.

The Raman spectra of 3 mol dm^{-3} $MgCl_2$ solution measured at 25 °C showed slight change in the pressure range of 0.1-45 MPa. At a constant pressure of 30 MPa reliable Raman spectra of 3 mol dm^{-3} $MgCl_2$ solution were not obtained above 100 °C, probably due to the formation of magnesium(II) chloride crystals.

Raman spectra and X-ray diffraction data measured at various temperatures and pressures will be presented.

E-P2

Diminution of hydrophobic effects at elevated temperatures and pressures.

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The study of P-V-T-x properties of solutions allows calculations thermodynamic properties. The following organic compounds were used as co-solvents: mononatomic alcohols (C_1-C_3), amides (formamide, N-methyl-, N,N-dimethylformamide, hexamethylphosphorictriamide, acetamide), nitriles (acetonitrile), ketones (acetone). The changes of thermodynamic properties of the aqueous mixtures with mentioned solutes as function of composition, temperature and pressure are discussed in report. The compressibility coefficients (β) and its relation with reorganization entropy at high temperatures and pressures have been studied. The diminution of hydrophobicity at elevated pressure and temperature for water-N,N,dimethylformamide, water – alkane and water-alcohol mixtures as examples is found to be nonlinear. For all of V=f(x) at water rich compositions (x~0,05) and high pressures the maximum is observed, which increases at low temperatures. This behaviour is discussed in the report within statement of the aqueous tetrahedrality increasing. Direct incorporating of tetrahedral correlation in liquid water provides accurate description of solvent re-organization with different temperatures and solute inclusions. The development here made a clear separation between entropic cost of solvation for short-range water-water correlation in a first shell of solute and bulk water structures. The presented in the report the model of solvent reorganization entropy is simple and related to modern theory of information and statistical mechanics itself instead of phenomenological approaches widely used for theory of liquids. Dependence of the reorganization entropy on temperature , as calculated from introduced approach are calculated and discussed.

This work was supported by RFBR, grants No 02-03-32285, 02-03-32287

E-P3

High-Pressure NMR Studies on Solute-Solvent Interactions in Supercritical Carbon Dioxide

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We have paid much attention to supercritical carbon dioxide (sc-CO_2), in particular as reaction media, because of its "green" nature. In order to promote applications of sc-CO_2, understanding of "CO_2-philicity" on the basis of solute-solvent interactions is of great importance. From such a standpoint, we have studied the solvation structure and rotational dynamics of solute molecules in sc-CO_2 by measuring solvent-induced chemical shifts and relaxation times over a wide range of temperature and pressure with our developed high-pressure NMR cell.[1-3] In this report, we present the rotational correlation times of solvent and some solute molecules, and discuss unique behaviors near the critical point from not only the static but also dynamic viewpoints. Moreover, we will refer to CO_2-philicity, especially fluorine-CO_2 interactions, on the basis of experimental results.

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E-P4

Temperature and Volume Dependence of the Viscosity of Water and Heavy Water at Low Temperatures

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Isotope effects, determined as a function of temperature and pressure for the viscosity and self-diffusion coefficients of the isotopomers of water and for the tracer diffusion of HTO in ordinary water and of DTO in heavy water, are analysed using the thermal offset hypothesis of Robinson and coworkers. Within experimental error, the best experimental data appear to be consistent with the hypothesis at temperatures below about 30 °C, extending into the supercooled region, where the pressure dependence of the transport properties most clearly shows effects due to the H-bonded structure of liquid water.

New measurements of the viscosity of ordinary and heavy water at pressures to 400 MPa and from 25 to -17.5 °C reveal that such a correlation is most exact when made as a function of molar volume (i.e. density) rather than pressure.

F-P1

Isotopic Effect on Phase Equilibria of Atomic Fluids and their Mixtures. Molecular Simulation, theory, and Experiment

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Vapor-liquid and vapor-solid isotopic fractionation of noble gases and their mixtures are studied by molecular-based simulation of atomic Lennard-Jones fluids [1]. The temperature dependence of the fractionation factors for $^{36}Ar/^{40}Ar$, $^{20}Ne/^{22}Ne$, $^{80}Kr/^{84}Kr$ and the composition dependence of the corresponding fractionation factors for binary $Ar-Kr$ mixtures as predicted by simulation are compared with the existing experimental data, to assess the accuracy of $\hbar^2$-order Kirkwood-Wigner free energy expansion for specific Lennard-Jones parameterizations. Predictions of the fractionation factors for other isotopic pairs, including $^{20}Ne/^{21}Ne$, and $^{132}Xe/^{136}Xe$ as well as tests of some premises behind the microscopic interpretation of the fractionation factors are also given.

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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F-P2

Dynamics of Ions in concentrated Electrolyte Solutions

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We present recent developments about the theory of electrolyte solutions. The dependence of the ion transport coefficients with respect to the concentration has been investigated since the pioneering works of Debye, Hückel and Onsager and it is still being studied with great activity. Despite all these efforts, there remains the need to develop a comprehensive theory of transport for concentrated solutions. The present work is a contribution toward this end. It propose a self-consistent theory which is able to describe the various equilibrium and transport properties of ions for concentrated solutions (1-2 mol L). Originally based on semi-phenomenological equations, the dynamics of ions can now be understood in terms of Brownian motion. The transport quantities have specially been obtained from three different approaches:

- A Smoluchowski/MSA theory gives the various transport coefficients for concentrated solutions. This analytical theory has been obtained after a careful analysis of the reference-frames and of the hydrodynamic interactions [1].
- It is consistent with Brownian dynamics simulations. The latter allows the problem to be solved numerically [2].
- The mode-coupling theory (MCT) given for self-diffusion explains the discrepancy between the short-time (QENS) and long-time measurements (NMR, tracers) [3].

These results agree with the Onsager limiting laws. They generalize the latter in the case of concentrated solutions (1-2 mol L). They are self-consistent, i.e. the same diameters are used to describe all the physical properties of the system, so that there is no adjustable parameter.

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F-P3

Modeling Electrolyte Mixtures

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When electrolyte solutions XQ and YQ are mixed together, the interaction between species X and Y, not present in pure solutions, comes into reckoning. Interestingly, however, thermodynamic properties of such mixtures can often be empirically »constructed« from the properties of the pure electrolytes XQ and YQ[1]. In this work Monte Carlo simulation and integral equation theory results on some aspects of thermodynamics of mixtures of electrolytes with common species are presented. Charge symmetric and charge asymmetric mixtures of primitive model electrolytes at ionic strength ranging generally from 10^{-4} to 2.0 M are examined[2]. The osmotic and activity coefficients were calculated and the obtained mixing coefficients[3,4] were compared with those extracted from the experimental data for KCl/NaCl, $MgCl_2$/NaCl, and $LaCl_3$/NaCl mixtures[5]. The mixing coefficients contain useful information about interactions in the system, and are very sensitive on the detailed modeling of the participating species. The semi-quantitative agreement between the experimental and theoretical data was obtained, suggesting usefulness of the simple continuum model for predicting the mixing coefficients.

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F-P4

Computer simulation study of the liquid/vapor interface of water-acetonitrile mixtures

Pál Jedlovszky

Abstract not recieved

F-P5

Molecular dynamics simulation of $MgCl_2$ and $CaCl_2$ in methanol

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Classical molecular dynamics simulation has been carried out on $CaCl_2$ and $MgCl_2$ in liquid methanol to study the solvation shell of the alkaline earth metal ions. *Ab initio* calculations have been used to determine the ion - methanol dimer potential surface, then new interaction pair potentials have been developed. After carrying out a 120 ps simulation on different concentrated solutions, six-eight methanol molecules have been found in the first shell of the calcium ion with a 2.4 Å Ca^{2+}-O distance. The magnesium was found six coordinated in the concentration interval investigated. In both cases well-determined second shells have also been observed. The coordination number of the chloride ion was 5.3 and no characteristic second shell has been found.

F-P6

A Theoretical Investigation of DMSO – Ion Clusters

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We have studied the solvation of small cations (Li^+, Be^{2+}) and some anions (Cl^-, I^-) by DMSO molecules. Molecular dynamics simulations of clusters with different numbers of DMSO molecules (one and two solvation shells as well as larger systems) were performed with the Car-Parinello method. We have analyzed the structure of the solvation shells of the DMSO molecules around the ions and the interactions of the DMSO molecules between each other. Some of these results are compared with data from quantum-chemical geometry optimizations. Dynamical properties like the flexibility of the clusters and its vibrational frequencies are also reported in the poster.

F-P7

X-ray Diffraction and Molecular Dynamics Simulations of Liquid DMSO and DMSO – LiI solutions

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We report results of molecular dynamics simulations (343 molecules in an NVE ensemble at ~300K) that have been performed on liquid dimethyl sulfoxide (DMSO) and on the system DMSO / Li^+ / I^-. We discuss the differences between the analytical pair potentials that we have developed for the interaction between these species and formerly used potential functions. In liquid DMSO, we find a slight preference for an antiparallel orientation of neighboring O-S bonds. For DMSO / Li^+ / I^-, a preliminary analysis shows that the both Li^+ and I^- ions coordinate to DMSO in a well-defined and rather rigid way. The structure of these complexes, the bulk phase and the pure liquid is investigated in terms of radial, angular and other distribution functions.

F-P8

Steric Effect of Tetraalkylammonium Ions Solvation

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In this report the possibility of solvent molecules – tetraalkylammonium (TAA) ions penetration have been studied by experimental and calculation methods. The density of seven tetraalkylammonium bromides have been measured in N,N-dimethylformamide (DMF). The limiting partial molar volumes ($\overline{V_2^0}$) for these salts have been obtained. It is shown that the dependence of the limiting partial molar volume of salts investigated on reciprocal radius of TAA ion can not be explain by electrostriction but good be agreed with structural changes related to the penetration of solvent molecules into the Van-der-Vaals volumes of TAA ions. The geometrical configuration and minimal energy of interaction for ion tetrabutylammonium - DMF pair and the first solvation shell of tetrabutylammonium ion as well were calculated in HF 6-31-G** basis set. The volumetric effect observed in experiment, can be studied on the base of comparison obtained configuration (Q-structure corresponding to minimum of the interaction energy) and, so called, V-structure. The estimation of V-structure has been performed though averaging-out atomic trajectories over molecular dynamics simulation process, while one has been performed at time-scale of hindered translations of the DMF, equal approximately of 0.3 ps. As results, the average distances between nitrogen atom of tetrabutylammonium ion and oxygen, nitrogen and carbon atoms of the DMF molecule have been calculated at given temperature. Finally, the difference between partial molar volumes of ions for two studied structures have been calculated and discussed.

This research was supported by the Ministry of Education of the Russian Federation (grants № E02-5.0-309).

F-P9

Combined Quantum and Statistical Mechanics to Calculate Thermodynamic and Structural Properties of Water and Hydrated Methane and Ethane

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We calculated the structure of pure liquid water via the combination of quantum and statistical mechanical methods. The structure and the charge distribution of a water molecule, which are calculated quantum mechanically, are used in the site-site Ornstein-Zernike (SSOZ) integral equation with the Hypernetted chain (HNC) closure relation in order to determine the pair correlation function of the central water molecule with its surroundings. The pair correlation function is needed for the determination of the external potential energy of the surrounding solvent in the Schrödinger equation. Since the parameters of the short-range potential (Lennard-Jones Potential) are found to be dependent on the partial charges of the interacting molecules, we developed functional dependencies which are parametrized according to experimental thermodynamic properties. The charge distribution calculated by quantum mechanics determines the LJ-parameters in the interaction energy function of the SSOZ equation in the iteratively solved combined process.

Thus we obtained a consistent model of the water molecule as solute as well as solvent. With this consistent water model we are able to reproduce a number of thermodynamic properties over a wide range of temperature.

The water model is also useful for the description of the hydration of a second component in the case of infinite dilution. As an example we discuss the hydration of methane and ethane. It is shown that the structure and the charge distribution of both compounds are only marginally altered in solution compared to the gas phase. The energies and entropies of hydration are near to the experimental ones over a temperature range from 10 to 40 °C.

F-P10

A quantum chemical study of the adsorption of halogenide ions from aqueous solutions at a Cd(0001) surface

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Specific adsorption of ions at metal electrodes is important in various electrochemical phenomena and remains in the focus of intensive experimental and theoretical studies. A new insight in the nature of specific adsorption can be achieved by combining traditional capacity measurements with quantum chemical models. We report here first results on the electrochemical adsorption of chlorine, bromine, and iodide-ions at the (0001) face of a cadmium monocrystallite. The cluster model was addressed to model three adsorption sites (on-top, hollow, and bridge) at the metal surface. Quantum chemical calculations were performed at the SCF and DFT (B3LYP) level. All species adsorbed from gas phase were found to reveal a noticeable charge transfer to the metal. The calculations predict the on-top site as the most favourable. The energy of adsorption increases in the order: $Cl^- < Br^- < I^-$.

The main emphasis was put on the modelling of solution effects. They were treated in two different ways. First, we added to the adsorption term related to the gas phase a “phenomenological” term describing the partial dehydration of the ion which was suggested by Schmickler [1]. Finally, the “competitive” adsorption of halogenide ions with small water clusters was considered as well. The account of solvation entails arising tangible features, which make the computational results closer to available experimental data.

This work was supported in part by RFBR (projects № 01-03-02006, 02-03-33284) and by WTZ project I.13/2001.

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G-P1

Determination of the Bromhexine Hydrochloride in Non-Aqueous Medium

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Bromhexine hydrochloride, which belongs to the mucolytic expectorant class, reacts with perchloric acid in non-aqueous medium in a quantitative reaction. In order to reduce titration error which is the result of rapid variations of the electrode potential on dropwise addition of perchloric acid to bromhexine hydrochloride in the classical titration method, in our procedure bromhexine hydrochloride is added in non-aqueous medium to perchloric acid using potentiometric detection technique. Determination of the equivalence volume is performed by two methods:

- Using the Hostteler-Roberts formula
- Graphically, after plotting the ΔE/ΔV values as a function of the volume of titrant added.

The derivated curves of the potentiometric titration of bromhexine hydrochloride with perchloric acid are presented. The described method is simple, rapid, reproducible and applicable in any testing and control laboratories for quantitative determination of bromhexine hydrochloride in diverse pharmaceutical preparations.

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G-P2

Laser-based Studies of Reactions of Free Radicals with Aromatic Compounds in Aqueous Solution

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Chemical reactions of the free radicals OH, NO_3 and NO_2 with polar aromatic compounds of importance for the tropospheric aqueous phase were investigated by means of direct laser-based methods.

The reactivity of the nitrate radical toward selected aromatic compounds in aqueous solution has been investigated, rate constants at 298 K for the reactions of NO_3 - radicals with several *ortho-* and *para-*substituted phenols were determined in the present study. The radicals were generated by laser photolysis of adequate precursors and the absorption signals in function of time of these radicals were detected. Nitrate radical can react by either electron transfer or H-abstraction mechanism with the compounds considered in this study. Both kinetic and thermodynamic aspects are treated.

Futhermore, the flash photolysis of nitrate anions at $\lambda = 248$ nm and peroxodisulphate anions at $\lambda = 351$ nm was used to study the oxidation process of phenol by OH / NO_2 and NO_3 / NO_2 in aqueous solution under different experimental conditions. Two different mono-nitrophenols (isomer *ortho-* and *para-*) and a dihydroxy derivative (2-hydroxyphenol) were identified as the main reaction products by means of HPLC-DAD-ED technique and their yields of formation where directly compared with the initial radical concentrations of OH, NO_2 and NO_3, respectively.

G-P3

Hydrogenation of aqueous lipid dispersions followed by MALDI-TOF mass spectrometry

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The properties of biomembranes can be altered by catalytic hydrogenation of the unsaturated fatty acyl moieties of their polar lipid constituents.[1] The common analytical tool for such hydrogenations is the gas chromatography of the fatty acid methyl esters (FAME-s) obtained by transmethylation of the membrane lipids. However, transesterification yields a combined mixture of FAME-s and the characterization of the reactivity of the *individual* lipids by this method is not possible.[2]

In the present work, mixtures of polar lipids were hydrogenated using the palladium*bis*(alizarin monosulfonate) catalyst and the product mixtures were analyzed by MALDI-TOF mass spectrometry in order to determine the individual reactivity of the constituent lipids. In their binary mixtures, dioleyl phosphatidyl choline and dioleyl phosphatidyl ethanolamine showed the same reactivity. Addition of cholesterol slowed down the hydrogenation of these two lipids by about the same extent. Conversely, in the mixture of lipids isolated from the thylakoid of the blue-green alga *Synechocystis PCC 6803*, monogalactosyl and digalactosyl diacyl glycerols (MGDG and DGDG, respectively) reacted twice as fast as sulpholipids (SL) and phosphatidyl glycerol (PG).

Acknowledgement: Financial support by the Hungarian National Research Foundation (OTKA T043365) is gratefully acknowledged.

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G-P4

A Molecular Approach to Remove Lead from Drinking Water

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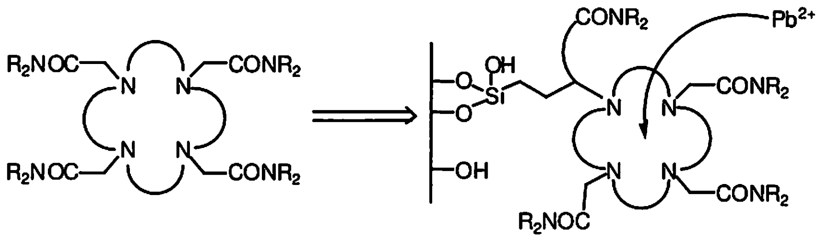
Exposure to lead-contaminated tap water is a persistent problem in most developed eastern countries, which primarily concerns children and the economically less-favored population. Once ingested through the gastrointestinal track, lead accumulates in vital organs and bones, and finally causes a number of diseases ranging from anemia to nervous system degeneration. Thus, the 1998 directive 98/83/CE of the Council of the European Communities relating to the quality of consumption water, recommends the national governments to promulgate an amendment intended to reduce the highest allowed lead concentration in drinking water from 50 μg L^{-1} to 25 μg L^{-1} on December 31, 2003 and to 10 μg L^{-1} in 2013.
In that context, we recently got involved in the design of a cartridge-based purification system that could be mounted directly on a kitchen faucet. Solid-phase extraction by covalent attachment of a lead-selective sequestering agent to the surface of silica gel was thought to be an efficient method.[1]



High binding affinity together with ion selectivity, especially with respect to alkaline and earth-alkaline cations, is of crucial importance. This fine-tuning is most conveniently achieved by taking advantage of the outstanding coordination properties displayed by *N*-functionalized tetraazamacrocycles of various sizes (12 to 14-membered rings) bearing amidic side chains.[2]
Both protonation and complex-formation constants with earth-alkaline and several transition and post-transition metals including lead have been determined in aqueous solution by potentiometry. The thermodynamic results pointed out the high stability of these ligands toward heavy metals. The lead-uptake efficiency of the macrocycles in natural fresh water has been investigated by extensive speciation calculations.
Finally, the efficiency of analogous ligands immobilized on silica gel to lower the lead concentration below the new parametric value has been evaluated by monitoring the lead concentration up and downstream a 50 g packed cartridge adapted to a 25 m long lead pipe. Field tests consisted in collecting 2 L tap water samples after a complete purge of the pipe followed by a 30 minutes stagnation time.

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G-P5

„IN VITRO" DISINTEGRATION STUDY AND CLONIDINUM DISSOLUTION IN WATER MEDIUM

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Was experimental determined:

1. Disintegration velocity of clonidinum palmets
2. Dissolution velocity of clonidinum, jellied
3. Allotment quotient between water medium and n-butanol
4. Transfer allotment through friate glass unselective membrane
5. Specific debit of transfer through unselective membrane

The experimental determination has the following conclusion:

1 Dissolving velocity in water of clonidinum is 400 mg/min

2 Water solubility at 20°C : 121,250 g, and butanol, at 20°C :120,000 g/l

3 Medium time of clonidinum pelmets is 4 minutes

4 Allotment coefficient water / n-butanol : 0,335

5 Transfer specific debit through friate glass membrane: 2,6025 $\mu g/cm^2 \cdot sec$

6 Clonidinum will be resip from stomach

G-P6

Application of macrocycle type molecules as chiral selector modifiers in capillary electrophoresis

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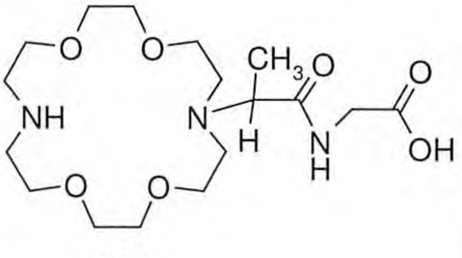
New diaza-crown ether derivatives (*R*-**1**, *RS*-**1**) have been synthesized from 1,4,10,13-tetraoxa-7,16-diazacyclooctadecan and tested as potential chiral selectors in capillary electrophoresis for chiral separation of five amino acid derivatives as commonly used building blocks in the synthesis of new chiral drugs. The individual use of the selectors did not lead to chiral differentiation. However, they enhanced the enantioselective effect of different cyclodextrins in dual selector systems by host-guest complexation (an example shown on Figure 1) and separation was observed. Here we report the effect of different substituted diaza-crown ether derivatives on the separation results obtained in dual systems with cyclodextrins.



RS-**1**

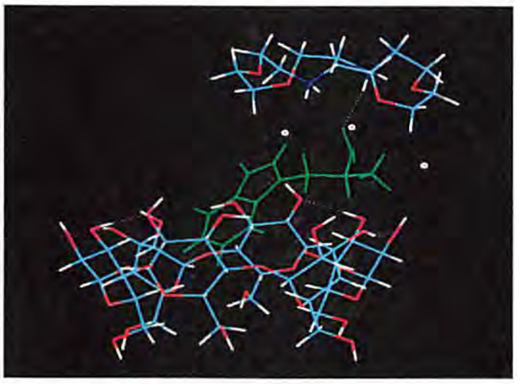


Figure 1

Acknowledgements
T. Iványi thanks the Ministry of the Flemish Community for the financial support (BIL 01/23). Financial support from the Hungarian Research Foundation (OTKA T 032100) is gratefully acknowledged. I. Lazar thanks the Bolyai János Research Schoolarship (BO/00452/99) for financial support. Y. Vander Heyden is a postdoctoral fellow of the Fund for Scientific Research (FWO) – Flanders.

G-P7

A Spectrophotometric Study on Amylose-Iodine Complex Formation in Aqueous and Nonaqueous Solvent

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The blue iodine-starch adsorption compound has found widespread application for determination of iodine or starch concentration in various samples as well as the colour indicator in iodimetric and iodometric methods. The nature of the coloured species has been the subject of much speculation and controversy.

In the present work the reaction between amylose and iodine has been studied by spectrophotometry in water and water containing varying proportions of nonaqueous solvents. It has been established that the characteristic blue complex exhibits a broad and asymetric absorption peak with its maximum near 600nm and a shoulder at about 480nm. The position and the intensity of the absorption bands depend on the amylose iodine ratio, presence of the iodide and the amount of the nonaqueous solvent added.

The increased iodide concentration is accompanied by corresponding shift in the positions of the UV/VIS absorption maxima. The amount of the nonaqueous solvent added remarkably reduces the intensity values around 600nm. In order to resolve overlapping peaks that appeared in the absorption spectrum, the derivatives of these spectra were analysed.

G-P8

Solvent Extraction of Uranium from Phosphoric Acid Using Different Extractants

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Abstract

Different extractants were used for separation of uranium from wet process phosphoric acid in batch wise process at laboratory scale. Solvent extraction of uranium from 5.4 M P_2O_5 phosphoric acid using PN-1200 was compared with uranium extraction from phosphoric acid using synergistic mixture of D_2EHPA+TOPO and synergistic mixture of D_2EHPA+TRPO. All extractants were diluted in normal kerosene. It is concluded that, PN-1200 has some good properties, such as high uranium distribution coefficient (Du), good stability, acceptable kinetics, good phase separation and simultaneous extraction of U^{+4} and U^{+6}.

G-P9

Macrocyclic chelators for intracellular applications

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Macrocycles form exceptionally stable complexes with the majority of transition and late transition metal ions including the lanthanides. Diagnostic use of the tetraaza macrocyclic complexing agent DOTA in MRI (magnetic resonance imaging) are widely known. Lately bismalonic acid derivative of diaza-tetraoxa macrocycle Kryptofix 2.2 has been proven to be able to selectively remove radioactive ^{90}Sr strontium ions from higher living organisms.

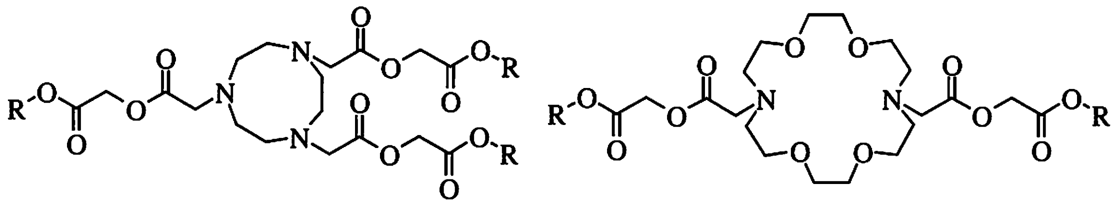

Figure 1 Structures of bio-hydrolysable ester derivatives of 1,4,7-triazacyclononane and Kryptofix 2.2

Here we present synthesis, characterization and hydrolytic properties of a series of new complexing agents based on 1,4,7-triazacyclononane and Kryptofix 2.2 which can be potentially used for the removal of highly toxic metal ions from the body.

Acknowledgements

Financial support from the Hungarian Research Foundation (OTKA T 032100) is gratefully acknowledged. I. Lázár thanks the Bolyai János Research Schoolarship (BO/00452/99) for financial support.

G-P10

Dipicolinic Acid and Its Calcium Salt as Biomarker Compounds Determined by Raman Spectroscopy

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Dipicolinic acid (2,6-pyridine dicarboxylic acid) is a universal constituent of bacterial spores where it represents 5-15% of total mass, and it has never been detected in vegetetive cells. Spores also contain high concentaration of calcium ions that are mostly complexed with dipicolinic acid in equimolar amounts. It was suggested that these compounds serve a role in the heat and ultraviolet irradiation resistance. Dipicolinic acid is often used as a signal of sporulating bacteria presence, and variety of analytical techniques have been employed for its detection, e.g. fluorescence, colorimetry, polarography, GC and HPLC. Most methods involve extraction and derivatization of dipicolinic acid that increase anaylsis time. In this work, Raman spectroscopy was used as a modern and fast analysis tool to detect the presence of dipicolinic acid in synthetic samples and also in samples contain bacterial spores. The Raman spectra of pure dipicolinic acid and its isolated calcium salt were asigned. Surface-enhanced Raman scattering (SERS) technique using silver colloids of different paricle size was employed to detect the presence of dipicolinic acid in solutions of low concentration range. The obtained spectra of dipicolinic anion was asigned and compared with spectra of solids. Applicability of biomaker compounds detection in pure culture of *Bacillus subtilis* by Raman spectroscopy was also discussed.

G-P11

Orientation-dependent Wertheim's theory for a two-dimensional model of water

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We develop an integral equation theory that applies to strongly associating orientation-dependent liquids, such as water. The theory is based on Wertheim's multi-density theory for associating fluids [1,2]. Water molecules are modelled as 2-dimensional Lennard--Jones disks with three hydrogen bonding arms arranged symmetrically, resembling the Mercedes-Benz (MB) logo [3]. In an earlier treatment, we developed a simplified version of this integral equation theory (IET) and tested it against the N,P,T Monte Carlo simulations [4]. The main approximation in the earlier calculation was an orientational averaging of the Mayer-function in the multi-density Ornstein-Zernike equation. Here we improve the theory by explicit introduction of an orientation dependence in the IET, based upon expanding the two-particle angular correlation function in orthogonal basis functions. We find that the new orientation-dependent IET yields a considerable improvement of the predicted structure of water, when compared to the Monte Carlo simulations. In particular, it predicts more long-range order than the original IET [5], with hexagonal symmetry, as expected for „hydrogen-bonded" ice in this model. The new theoretical approximation still errs in some subtle properties; for example, it does not predict liquid water's density maximum with temperature or the negative thermal expansion coefficient.

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G-P11

Determination of Iridium(IV) by Fluorescence Quenching of Esculin

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The determination of iridium is not a common analytical problem. Owing to their corrosion-resistant nature, iridium alloys have found a wide range of applications in both the chemical industry and the manufacture. Since iridium is usually present in such materials at low concentrations, methods with reasonably high sensitivity are required. In addition, iridium is usually present in association with other platinum metals. Therefore, successful determination of iridium can be performed only by analytical methods having high selectivity. Fluorescence quenching method was developed for determination of microamounts of iridium(IV) by using esculin as a new fluorescent probe. In 15 % methanol-water mixture esculin showed maximum excitation and emission wavelengths at 335 nm and 455 nm, respectively. The fluorescence of esculin was significantly quenched by iridium(IV). Under optimal conditions, iridium(IV) in the range 58-960 ng/ml can be determined. Most anions and cations do not interfere, even when present in large excess. Relative standard deviation of five measurements is 2,5 % for 500 ng/cm^3 Ir(IV). The quenching rate constant was determined using the Stern-Volmer equation.

The proposed method has been applied successfully for the determination of iridium(IV) in a series of synthetic mixtures.

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