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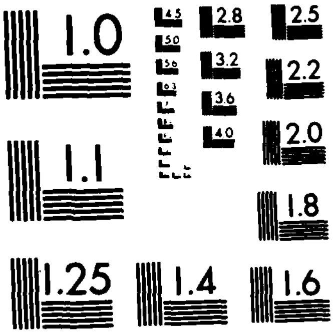

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AD-A158 830

Seventh International Symposium
on
Solute-Solute-Solvent Interactions

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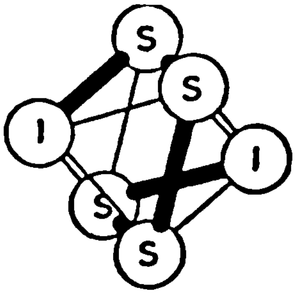

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7th INTERNATIONAL SYMPOSIUM ON SOLUTE-SOLUTE-SOLVENT INTERACTIONS

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PROGRAMME FOR 7TH ISSSSI

	MONDAY 15	TUESDAY 16		WEDNESDAY 17		THURSDAY 18		FRIDAY 19	
9.00 - 10.00	ARRIVAL	Plenary 2		R.A. Robinson Lecture		Plenary 3		Plenary 4	
9.00 - 10.00		Prof. J.E. Enderby		Dr. K.H. Khoo		Prof. P. Laszlo		Dr. J.-C. Justice	
10.00 - 10.20		Session 2 Rossky	Session 3 Franck	Session 4 Barthel	Session 3 Abraham	Session 4 Woolf	Session 1 Whitfield	4 - 11	3 - 13
10.20 - 10.40								4 - 12	3 - 14
10.40 - 11.10		COFFEE		COFFEE		COFFEE		COFFEE	
11.10 - 11.30		2 - 5	5 - 5	2 - 15	5 - 9	4 - 7	1 - 1	4 - 13	3 - 15
11.30 - 11.50		2 - 6	5 - 6	2 - 16	5 - 10	4 - 8	1 - 2	4 - 14	3 - 16
11.50 - 12.10		2 - 7	5 - 7	2 - 17	5 - 11	4 - 9	1 - 3	4 - 15	3 - 17
12.10 - 12.30		2 - 8	5 - 8	2 - 18	5 - 12	4 - 10	1 - 4	Closing talk Prof. Wood	

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	LUNCH		LUNCH			LUNCH	LUNCH		LUNCH
2.00 - 2.20			2-9	3-1	4-1	FREE	2 - 19	3 - 7	DEPARTURE
2.20 - 2.40	Plenary 1 Prof. R.H. Wood		2-10	3-2	4-2		2 - 20	3 - 8	
2.40 - 3.00			2-11	3-3	4-3		2 - 21	3 - 9	
3.00 - 3.20			2-12	3-4	4-3		2 - 22	3 - 10	
3.20 - 3.40	Session 2 Heinzinger	Session 1 Millero	2-13	3-5	4-5		2 - 23	3 - 11	
3.40 - 4.00			2-14	3-6	4-6		2 - 24	3 - 12	
4.00 - 4.30	TEA		TEA				TEA		
4.30 - 4.50	2 - 1	5 - 1	POSTER 1				POSTER 2		
4.50 - 5.10	2 - 2	5 - 2							
5.10 - 5.30	2 - 3	5 - 3							
5.30 - 5.50	2 - 4	5 - 4							

Themes presented at the 7th International Symposium on Solute-Solute-Solvent Interactions include:

SESSION LECTURE - THEME 1

THE PHYSICAL CHEMISTRY OF NATURAL WATERS

Frank J. MILLERO

Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida 33149, U.S.A.

A knowledge of ionic interactions is necessary to understand the chemical processes that occur in natural waters such as rivers, lakes, estuaries, seas and ocean waters. Short-range ion-water and ion-ion interactions have been shown to affect equilibrium processes (acid-base, solubility, oxidation-reduction) as well as the physical-chemical properties of natural waters. Since ionic interactions affect the state of metal ions, many have suggested that biological activity is affected by ionic interactions. Recent work has also shown that ionic interactions can affect the rates of chemical processes in natural waters.

The ionic interaction models used to account for these interactions will be examined. Simple additivity models are used to estimate the density and sound speed of the mixtures of sea salts and seawater. The estimated values are shown to be in good agreement with the measured values. The ion pairing and specific interaction models are used to estimate the activity coefficients of ions in seawater and brines. The results are shown to be in good agreement with measured values. The estimated activity coefficients are shown to yield reliable values of the pK_a's for the ionization of acids.

SESSION LECTURE - THEME 1

CHEMICAL SPECIATION IN NATURAL WATERS - A CAUTIONARY TALE

Michael WHITFIELD, *Marine Biological Association of the UK,*
The Laboratory, Citadel Hill, Plymouth PL1 2PB, U.K.

Speciation studies in natural waters have revealed a number of shortcomings in the application of the traditional equilibrium approach. Even where complete equilibrium can be assumed and only dissolved inorganic species are involved, considerable uncertainties remain in many of the stability constants for complexation, hydrolysis and protonation equilibria. The application of such calculations is also restricted since most work has been at 25 °C and 1 atmosphere pressure - conditions typical of tropical surface waters. Despite such difficulties, the tendency has been for a proliferation of modelling exercises, with species distributions often quoted to a few tenths of a per cent, instead of a systematic comparison of model predictions with experimental measurements.

Realistic equilibrium calculations must also take account of the interactions of dissolved species with colloidal material and with (frequently uncharacterised) organic ligands. Problems concerned with distributions of complexing sites with varying properties must be recognised in assessing the importance of such equilibria. Also, many chemical systems are pushed far from equilibrium by biological and photochemical processes so that account must be taken of the presence of metastable components and of the rate with which such species attain their equilibrium state. Examples are provided by the presence of the reduced forms of many elements in air-saturated waters.

To sidetrack some of these problems, numerous 'operational' procedures have been developed which divide the total element concentrations into various fractions by techniques such as filtration, ion-exchange and u.v. irradiation. Since the total concentrations of many elements may not exceed 10^{-9}M, such procedures are prone to experimental error. In addition, their relationship to the molecular concept of speciation is not always clear. A re-assessment is required of our approach to chemical speciation studies that will provide a much closer link between the processes we intend to study and the procedures we use for elucidating the chemistry of the elements in natural waters.

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PLENARY LECTURE - THEME 2

IONIC HYDRATION BY NEUTRON SCATTERING

J.E. ENDERBY
H.H. Wills Physics Laboratory, University of Bristol,
Bristol BS8 1TL, ENGLAND

The method of difference applied to neutron diffraction data obtained from isotopically different aqueous solutions is described. It is shown that the method allows a detailed description of ionic hydration to be given. Several examples of the technique are discussed.

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SESSION LECTURE - THEME 2

MOLECULAR DYNAMICS SIMULATIONS OF AQUEOUS ELECTROLYTE SOLUTIONS

K. HEINZINGER
Max-Planck-Institut für Chemie (Otto-Hahn-Institut) Mainz, F.D.R.

The MD simulations have been performed with the ST2 and an improved Central Force model for water. The ion-water pair potentials are either calculated by modelling the ions as Lennard-Jones spheres with an elementary charge at the centre or based on *ab initio* calculations. The concentrations ranged from 0.55 to 2.2 molal with 200 water molecules in the basic periodic cube. The simulations extended over 10 ps.

The structural properties of the solutions are discussed on the basis of radial distribution functions, the orientation of the water molecules and their geometrical arrangement in the hydration shells of the ions. The dynamical properties are calculated from various autocorrelation functions. Results are presented for the influence of the ions on self-diffusion coefficients, relaxation times, hindered translations, librations and internal vibration of the water molecules.

Contd

SESSION LECTURE - THEME 2

THEORETICAL STUDIES OF AQUEOUS SOLUTION STRUCTURE

[illegible]

Peter J. ROSSKY

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712 U.S.A.

Computer simulation and, more analytical, integral equation methods can be applied to the problem of elucidating the detailed structural properties of strongly interacting molecular solutions of genuine chemical significance. The more analytical, extended RISM, approach can provide such results in a computationally convenient way not yet available via simulation. The success of such current statistical mechanical approaches in describing aqueous solutions is considered through three examples: the structure of liquid water as a function of hydrogen bond strength, the potential of mean force between atomic ions in an aqueous medium, and the aqueous solvent effect on the reaction free energy surface for the SN2 reaction of chloride with methyl chloride.

PLENARY LECTURE - THEME 3

LOCAL ORDER DUE TO ELECTROSTATIC INTERACTIONS

Pierre LASZLO
Department of Chemistry, University of Liège, BELGIUM

The talk will survey ion-dipole and anion-cation interactions such as ion pairing, ionic solvation, counter ion binding and condensation around a polyelectrolyte. Results obtained by a variety of experimental methods, but predominantly by nuclear magnetic resonance methods, will be discussed. They have been obtained for systems having the symmetry of a cylindrical rod, of a sphere, and of a plane. The following questions will be addressed:

(i) consistency between the timescale of molecular dynamics in solution and a chemical equilibrium description;

(ii) the empirical equivalence between conceptually opposed models, such as mass action law binding and Poisson-Boltzmann condensation; and the few experimental criteria available for a distinction;

(iii) the importance of the fractal dimension (in the sense of Mandelbrot theory) in determining diffusion rates and reaction kinetics between partners evolving on an irregular and self-similar surface.

SESSION LECTURE - THEME 3

AQUEOUS MIXTURES TO SUPERCRITICAL TEMPERATURES AND AT HIGH PRESSURES

E.U. FRANCK
Institute of Physical Chemistry, University of Karlsruhe,
Kaiserstrasse 12, D 7500 Karlsruhe, WEST GERMANY

Thermophysical properties of dense supercritical water with special emphasis on dielectric permittivity are discussed. Phase diagrams and some critical curves of the binary systems H_2O-H_2, H_2O-N_2, H_2O-O_2, H_2O-CH_4 and H_2O-He to 450 °C and 200 MPa are shown. H_2O-He has a type I critical curve. A rational equation of state to calculate phase diagrams and critical curves for polar-non polar systems is described. Measurements with the ternary system H_2O-CH_4-NaCl are presented. 2 mol per cent of added NaCl shifts the phase separation H_2O-CH_4 by 100 degrees to higher temperatures. The excess Gibbs energy for homogeneous supercritical H_2O-N_2 mixtures to 200 MPa is shown. The static permittivity of super-critical H_2O-benzene mixtures is presented as an example of dielectric behaviour of polar-non polar mixtures in general.

SESSION LECTURE - THEME 3

SOLVENT EFFECTS ON REACTION RATES

Michael H. ABRAHAM, *Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, U.K.*

Most work on solvent effects on rates of reaction has involved the correlation of log k or of $\Delta G^{\ddagger}$ with various properties or parameters characteristic of the solvent, or single linear regressions. In another method of analysis, the solvent effect on $\Delta G^{\ddagger}$ dissected into initial state and transition-state contributions, and is followed, where possible, by a comparison of the solvent effect on the transition-state with that on a suitable model solute. Previous such work on simple S_N1 or S_N2 reactions will be reviewed, and it will be shown that both methods lead to essentially the same conclusions with respect to such transition-state properties as dipole moment and charge separation.

More recently, the method of multiple linear regression has been used to correlate log k or $\Delta G^{\ddagger}$ with solvent properties or parameters. The application of this method to S_N1 and S_N2 reactions using the solvatochromic parameters of Kamlet and Taft (π^*,α,β) will be considered, and a comparison will be made of transition-state properties obtained from the Kamlet-Taft procedure with those obtained by the method of model solutes.

THEORIES OF TRANSPORT PROPERTIES USING THE ONSAGER TREATMENT

Jean-Claude JUSTICE
Laboratoire d'Electrochimie, Université Pierre et Marie Curie,
4 Place Jussieu, 75230 Paris Cedex 05, FRANCE

The fundamental equations of the Onsager approach of transport properties in linear response are summarized. From a reformulation of the part of the ion pair distribution function which is perturbed by the ionic velocities, an echo formulation for trace diffusion is derived which can be compared with former similar results obtained for conductance. It clearly appears that these two different transport processes are in agreement with the original Bjerrum formulation of ionic association for excess thermodynamic properties at equilibrium which can be derived from the Mayer activity expansion.

It is finally shown how the Pikal equation for chemical diffusion can be reformulated to reach a final expression also in complete agreement with a Bjerrum formulation. The improvement in overall efficiency of these echo formulations for ions of higher charges and for solvents of lower dielectric constants is emphasized as well as their evident ability to be easily extended to more realistic models for ionic interactions than the restricted primitive model.

SESSION LECTURE - THEME 4

DATA ON TRANSPORT PROPERTIES OF ELECTROLYTE SOLUTIONS FOR APPLIED RESEARCH AND TECHNOLOGY

J. BARTHEL and H.-J. GORES
Institut für Physikalische und Theoretische Chemie der Universität Regensburg, 8400 Regensburg, F.R.G.

Transport properties, conductance of electrolyte solutions and viscosity of their solvents, as well as dielectric properties are discussed in the framework of applications in modern technology. Electrolyte solutions in high energy batteries with lithium anodes are chosen for exemplifying both the role of the solvent and the fulfilment of supplementary conditions imposed by technical applications. The generation of electrolyte property profiles by means of a data base is used and a new data and method base for electrolyte solutions, ELDAR, is presented.

SESSION LECTURE - THEME 4

INSIGHTS INTO SOLUTE-SOLUTE-SOLVENT INTERACTIONS FROM TRANSPORT PROPERTY MEASUREMENTS WITH PARTICULAR REFERENCE TO METHANOL-WATER MIXTURES AND THEIR CONSTITUENTS

L.A. WOOLF

Atomic and Molecular Physics Laboratories, Research School of Physical Sciences, Australian National University, Canberra, AUSTRALIA

Interactions in methanol-water solutions for pressures up to 280 MPa in the temperature range 278-323 K will be examined using experimental measurements of the following:

1. self-diffusion coefficients of the pure components and some isotopically-substituted compounds;

2. diffusion in methanol-water mixtures;

3. shear viscosities;

4. excess thermodynamic and related properties for both methanol-water and acetonitrile-water mixtures.

The data present will be used to show

(a) unusual isotope effects in both methanol and water;

(b) temperature, pressure and composition dependence of interactions in methanol-water mixtures compared to those of a reference mixture (acetonitrile-water);

(c) velocity correlation coefficients for the mixtures.

R.A. ROBINSON MEMORIAL LECTURE

IONIC INTERACTIONS IN AQUEOUS MIXTURES OF HYDROCHLORIC ACID WITH DIVALENT METAL CHLORIDES

Kean H. KHOO

Department of Chemistry, University of Malaya, Kuala Lumpur, MALAYSIA

The activity coefficient of hydrochloric acid has been studied and, in some cases, re-examined in binary mixtures with divalent metal chlorides in aqueous solutions. Precise measurements have been made using silver-silver chloride and hydrogen electrodes in cells without liquid junction. These results have been successfully interpreted in terms of the equations developed by Pitzer in 1973, using only two interaction parameters, one for cation-cation doublet (θ), and the other for cation-anion-cation triplet (ψ), interactions. When ions of the same sign but different charges are mixed, there will be contributions to the excess Gibbs energy from higher-order electrostatic terms beyond the Debye-Hückel approximation which may, however, be indistinguishable from the effects of short-range forces. When these effects are accounted for in the manner proposed by Pitzer, a significant improvement in the fit of the experimental data is obtained without having to increase the number of parameters. θ and ψ could be expected to depend upon the divalent metal cation. However, if highly precise values of activity coefficients were not desired, it is possible to simplify the Pitzer treatment by setting ψ equal to zero and representing all the $HCl + MCl_2 + H_2O$ systems by a single value of ϕ.

THEME 1

Fundamental and applied aspects of naturally-occurring electrolyte solutions (natural waters, brines, etc.)

ORAL CONTRIBUTIONS

1-1 (O) ELECTROLYTE SOLUTIONS NEAR THE CRITICAL POINT OF WATER

David J. TURNER
Central Electricity Research Laboratory, Kelvin Avenue,
Leatherhead, Surrey, UK.

All ions in a solution exert a compressional influence on the solvent molecules in their vicinity. When the solvent has a high compressibility, as it will near its critical point, the effect is expected to be very large, especially at low concentrations. [1] It manifests itself in both the thermodynamic and transport properties of the ions.

Reported data on apparent molal volumes, molal compressibilities, heat capacities, excess entropies and conductance for NaCl solutions show the effects of the large electrostriction. For illustrative purposes, some of the data are rationalised using a very crude two-state model which treats the solvent either as fully compressed by the ions or as free solvent.

The microscopic inhomogeneity implied may explain a reported gravity influence on the conductance of a super-critical salt solution. [2] This possibility, in part, led to a proposal to make similar measurements under conditions of low gravity. Preliminary results will be described.

1. Turner, D.J. *Thermodynamics of Aqueous Systems with Industrial Applications. A.C.S. Symposium Series* No 133, p.653, (1980).
2. Corwin, J.F., Bayless, R.O. and Owen, G.E., *J. Phys. Chem.* 64, 641 (1960).

1-2 (O) SPECIFIC HEAT CAPACITIES OF PURE WATER AND SEAWATER AT HIGH PRESSURES

Chen-Tung Arthur CHEN*
College of Oceanography, Oregon State University,
Corvallis, Oregon 97331, U.S.A.

Equations of state for pure water and seawater were used to calculate high-pressure specific heat capacities at constant pressure (C_p), and at constant volume (C_v). Equations are given to represent the pure water C_p and C_v values over the temperature range of 0 to 100 °C and pressure range of 0 to 1000 bars. Equations are also given to represent the seawater C_p and C_v values over the salinity range of 0 to 40×10^{-3}, temperature range of 0 to 40 °C and pressure range of 0 to 1000 bars. These equations agree with the direct measurements reported in the literature for pure water to within 0.1% over the measurement ranges of 20 to 40 °C and 50 to 500 bars. No direct high-pressure seawater measurements are available for comparison.

*Work completed while visiting the National Sun Yat-sen University, Taiwan, The Republic of China.

1-3 (C) SINGLE ION ACTIVITIES IN STRONG SALT SOLUTIONS OF RELEVANCE TO MINERAL CHEMISTRY

David M. MUIR and Gamini SENANAYAKE
School of Physical Sciences, Murdoch University,
Perth, Western Australia 6150, AUSTRALIA

The activity of ions and salts in solutions of high ionic strength is significantly different from that in dilute solutions and cannot be predicted by the Debye-Hückel or Davies equations. In recent years, several empirical equations have been proposed to calculate mean ionic activities in concentrated solutions and hydration theory now rationalises the large increases in activity in terms of the activity of free water and the hydration number of the electrolyte. However, single ion activities are potentially more useful to hydrometallurgists because they can rationalise changes in redox potentials, stability constants, solubility etc.

Single ion activities in strong salt solutions are most conveniently determined either directly or indirectly by e.m.f. measurements and correcting for the liquid-junction potential E_J. Values of H^+, Cl^-, SO_4^{2-} and various metal ions relevant to hydrometallurgy are reported and compared in chloride and perchlorate media of high ionic strength. A comparison is also made between ions in salt solutions and mixed aqueous organic solutions.

Reference: To be presented and published (in part) in "Extraction Metallurgy '85" Proceedings of Conference, Institute of Mineral Metallurgists, London, September 1985.

1-4 (O) THE PREDICTION OF SCALE FORMATION IN OILFIELD BRINES

Gordon ATKINSON, Betty L. ATKINSON, Krishnam RAJU
Department of Chemistry, The University of Oklahoma,
Norman, OK 73019, U.S.A.

In the production of petroleum and natural gas, problems are often caused by the brines found in almost all reservoirs. These brines are ancient seawater that has been equilibrating with its reservoir matrix for eons. When the petroleum or gas is produced the brine accompanies it to the surface. The most common problem is "scale" formation - the precipitation of natural minerals in the pipes and surface equipment. This is caused by the changing temperature and pressure conditions.

The problems of predicting "scale" formation is, from a thermodynamic point of view, the problem of predicting the solubility of a mineral as a function of temperature, pressure, and the presence of "inert" salts. We have approached this problem using standard thermodynamic techniques together with the Pitzer formalism for activity coefficients and water activity. The approach is very successful over wide ranges of temperature, pressure, and salt concentration. The calculational approach is illustrated with examples of $BaSO_4$, $SrSO_4$, and $CaSO_4 \cdot 2H_2O$ solubility calculations. Certain complexities in the approach are noted.

[illegible]

THEME 2

Structual determination of the properties of liquids and solutions (molecular dynamics, scattering studies, Monte Carlo methods and spectroscopic studies);

ORAL CONTRIBUTIONS

Cont'd pg. 3-1

P-1 (O) MOLECULAR DYNAMIC SIMULATION OF LIQUID WATER

G.C. LIE and Enrico CLEMENTI
IBM Corporation, Dept. 48B/MS 428, Neighbourhood Road, Kingston, New York 12401, U.S.A.

The widely used ab initio CI potential for water-water interaction [1] has been extended to include the effect of the intramolecular vibrations of the water molecules. The extended MCY potential is then used in a molecular dynamic simulation to study some equilibrium and dynamical properties of liquid water at room temperature. The average intramolecular OH bond distance in the simulated liquid state is found to be 0.017 A longer than that of the isolated water molecule, whereas the HOH angle is 1.1° smaller. The high pressure, 8000 atm, reported for the original MCY potential [2,3] has been drastically reduced in the present simulation. Other properties, such as radial distribution functions, heat capacities, and spectrum densities, etc. will also be discussed.

1. O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, 64. 1351 (1976).
2. G.C. Lie, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, 64, 2314 (1976).
3. G. Corongiu, private communication.

2-2 (O) ORIENTATIONAL CORRELATIONS IN WATER AND AQUEOUS SOLUTIONS

G. PALINKAS and K. HEINZINGER
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Saarstr. 23, D-6500 Mainz, F.R.G.

The invariant expansion of the water-water and ion-water site-site structure functions has been studied by molecular dynamics simulation of pure ST2 and CF water and several aqueous alkali halide solutions. The orientation of water molecules next to the ions and their mutual orientation in the hydration shells as well as the residual solvent structure have been investigated by means of $g_{\mu\nu}^{mnl}(r)$ expansion coefficients.

The molecular symmetry requirements produce a considerable reduction in the number of non-vanishing coefficients in the expansion of the oxygen-hydrogen and ion-hydrogen site-site correlation functions. Consequently a smaller number of coefficients was sufficient to reach convergence. The role of hydrogen bonding and the effect of the ion size in the orientational correlations of the systems have been investigated. Also the applicability of the formalism for the analysis of scattering experiments will be discussed.

2-3 (O) A MOLECULAR DYNAMICS SIMULATION STUDY OF AN AQUEOUS LiI SOLUTION BETWEEN FIXED WALLS

E. SPOHR and K. HEINZINGER
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Saarstr. 23, D-6500 Mainz, F.R.G.

The results of a molecular dynamics simulation study of 16 ions and 200 water molecules between two fixed walls corresponding to a 2.2 molal aqueous LiI solution are presented. The simulation extended over 10 picoseconds near room temperature. The water molecules are modelled by the ST2 model introduced by Stillinger and Rahman [1] and the ions as Lennard-Jones spheres with an elementary charge at the centre.

The strong ion-water interactions disturb the oscillatory behaviour of the oxygen density profile in the central part of the lamina caused by the structure-making effect of the walls and found for pure water. [2]

Further structural and dynamical properties are calculated separately for layers having a thickness of approximately one molecular diameter. The solvent structure near the interface is discussed by presenting pair correlation functions and orientational distribution functions and comparing these to the corresponding functions in an isotropic LiI solution [3] and in pure water between walls, respectively.

Velocity autocorrelation functions and spectral densities of hindered translational motions are also given separately for the interphasial and the central region of the lamina.

1. F.H. Stillinger and A. Rahman, *J. Chem. Phys.* 60, 1545 (1974).
2. R. Sonnenschein and K. Heinzinger, *Chem. Phys. Lett.* 102, 550 (1983).
3. Gy. I. Szasz, K. Heinzinger and W.O. Riede, Z. *Naturforsch.* 36a, 1067 (1981).

2-4 (O) SOLUTE-SOLUTE-SOLVENT INTERACTIONS IN AQUEOUS SOLUTIONS OF FORMAMIDE AND UREA

P. AMODEO, G. BARONE, V. BARONE, P.L. CRISTINZIANO and F. LELJ
Department of Chemistry, University of Naples, via Mezzocannone 4,
I-80134 Naples, ITALY

The properties of aqueous solutions of polar non-electrolytes are of interest, particularly those of moderately to strongly concentrated solutions, where solute-solute and solute-solvent interactions are of comparable magnitude and both give significant contributions to the overall properties. We are making a theoretical study of the binary mixtures formamide + water and urea + water based on the determination of energy minima for medium-size clusters and Monte Carlo simulations for a pair of solute molecules either insulated or interacting with a limited number of water molecules. Because of the large number of particles involved, empirical effective two-body potentials are used, selected on the basis of preliminary studies on the different pairs of molecules and on the comparison with experimental data and quantum-mechanical computations. Only the potential functions proposed by Lifson give good results both for the interaction energies and the equilibrium geometries of the dimers water-water, formamide-water and urea-water; in particular the NH--OC hydrogen bridge is more stable than both $NH{-}{-}OH_2$ and CO--HOH and the energies for the formation of the hydrogen bridges CO--HOH + $NH{-}{-}OH_2$ from one side and NH--OC + $H_2O{-}{-}HOH$ from the other side are very similar. Furthermore, the limiting value of the interaction energy per water molecule (obtained from clusters containing up to 21 molecules) is in good agreement with the experimental value (9 - 10 kJ mol^{-1}). Optimization of clusters containing one amide molecule and an increasing number of water molecules shows that the first hydration shell contains four water molecules for formamide and five water molecules for urea. Finally for clusters containing two solute molecules, it has been found that energy minima correspond to vicinal dispositions of the two solute molecules with a relative disposition very different to that of the insulated dimer. In particular there is no evidence of solute-solute hydrogen-bridges and the minimum energy structure is rather determined by the contemporary optimization of solute-solvent and solvent-solvent interactions.

2-5 (O) DYNAMICS OF DIELECTRIC ENRICHMENT IN SOLVENT MIXTURES

Paul SUPPAN
Institute of Physical Chemistry, University of Fribourg,
CH-1700 Fribourg, SWITZERLAND

In binary mixtures of solvents of different dielectric polarities,the local distribution in the field of solute dipoles and monopoles can be quite different from the bulk distribution; the mole ratio of polar to non-polar solvent in the solvent shell ($Y = y_P/y_N$) is related to the bulk mole ratio ($X = x_P/x_N$) by the index of preferential solvation Z: $Y = X\ e^Z$. Z depends on the solute molecule's electric charge or dipole moment, on its molecular volume and on the solvents' dielectric constants.

The redistribution of solvent mixtures in the field of solute molecules requires the diffusion of the solvents. The dynamics of this redistribution around suddenly-created monopoles and dipolar excited molecules has been investigated as a function of solute and solvent parameters, viscosity and temperature. In low-viscosity organic solvents near 300 K, dielectric enrichment is complete within a few hundred ps, this time increasing rapidly with solvent viscosity. The dynamics of solvent redistribution can be observed by time-resolved fluorescence spectroscopy and flash photolysis of which a few examples are discussed.

It is shown that in general the kinetics of dielectric enrichment can be treated as diffusion-controlled encounters of the solute and the polar solvent. Electric field enhanced diffusion may become important for some very large dipoles and for monopoles when the polar solvent molecules also have large dipole moments (e.g. acetonitrile, 4 D).

K.S. Nitsche and P. Suppan, *Chimia* 36, 346 (1982).

2-6 (O) DYNAMIC HYDRATION STRUCTURE IN DILUTE AQUEOUS SOLUTIONS OF NONELECTROLYTES

Koichiro NAKANISHI, Hideki TANAKA and Tatsuo ISHIBASHI
Department of Industrial Chemistry and Division of Molecular Engineering, Kyoto University, Kyoto 606 JAPAN

Molecular dynamics calculations have been carried out for dilute aqueous solutions of t-butanol (TBA), urea and purine in an NTV ensemble. All the pair potentials used are from quantum mechanical *ab initio* LCAO SCF MO calculations for dimers. The total number of molecules and the temperature of the solution were 216 and 298.15 K, respectively. Experimental density values were used to determine the cell size. Molecular dynamics runs have been extended up to 70,000 time steps (equivalent to 20 - 30 picoseconds) with a time step of 6 x 10^{-4} ps. The main results from the analysis of dynamic data are as follows.

1. TBA molecules show "solvent-separated" self-association (hydrophobic interaction) even in as dilute a region as 3 mol% solution.

2. "Iceberg" formation and a relative decrease in the self-diffusion of water around TBA have been observed with no hydrogen bonding interaction between TBA molecules.

3. Urea molecules show a strong tendency to self-association in 8 mol% solution, though there is no appreciable structuring of water and the decrease in the self-diffusion of water is smaller than that in 3 mol% TBA solution.

4. The purine-water potential surface has a peculiar feature and the motion of water near the hydrophobic region of purine is highly cooperative.

Other results include internal energies, radial distribution functions and various time correlation functions and lead to a unified interpretation of the behaviour of nonelectrolytes in dilute aqueous solutions.

2-7 (O) COMPUTER SIMULATION OF AMINO ACID AND NUCLEIC ACID SOLUTIONS

Julia M. GOODFELLOW and P. Lynne HOWELL
Department of Crystallography, Birkbeck College, University of London, Malet Street, London EC1 7HX, UK

Both proteins and nucleic acids require water for their stability and for their ability to function. We have used Monte Carlo computer simulation techniques to study the molecular structure and energetics of water around (i) polar amino acids such as serine and threonine, (ii) apolar amino acids such as glycine, leucine, valine and alanine, (iii) charged amino acid side chains such as arginine and (iv) a dinucleotide (dCpG) in solutions of pure water and water plus various different counter-ions (e.g. Na^+, Ca^{++}).

The analysis of the simulation data has been used to look for changes in the properties of water molecules in these solutions compared with the same property in simulated 'bulk' water. Thus, when average properties for water molecules in solution were calculated, it was seen that the insertion of any amino acid leads to (i) an increase in the linearity of the water-water hydrogen bonds, (ii) a slight change in the water molecule dipole moment and (iii) a larger distribution (standard deviation) around the mean value for the dipole moment and energies of the water molecules. The average and instantaneous structure of water around both polar and apolar solute atoms have investigated using computer graphics, in order to look for similarities in the patterns of hydration around e.g. all polar -OH groups or all apolar $-CH_3$ groups.

Similar procedures are being used to analyse solvent around a dinucleotide (two base pairs in the B helical conformation) in solution in order to define the hydration patterns associated with the backbone phosphate groups and with the polar groups along the edges of the base pairs in the minor and major grooves of the helix. The accessibility of these groups to solvent is known to change in the transition from the 'B' to 'A' helical conformation. We are also investigating the changes to these hydration patterns with the addition of counter-ions.

2-8 (O) MOLECULAR INTERACTIONS IN BIOLOGICAL SYSTEMS

Steven CHIN and Enrico CLEMENTI
IBM Corporation, Dept. 48B/MS 428, Neighbourhood Road, Kingston, New York 12401, U.S.A.

Molecular interactions in systems of biological interest, for example, a DNA helix or a large protein molecule, play an important role in determining the structure and function of those molecules which comprise these systems (nucleic acid bases in DNA and amino acids in proteins). The influence of the chemical environment on some of the physical and chemical properties of a DNA helix and a protein fragment have been examined by performing computer simulations. For the DNA helix, the influence of the attached sugar and phosphate groups, counter-ions, and solvent have been investigated. In the case of the protein fragment, the influence of the solvent on the stability of different conformations has been modelled.

2-9 (O) WATER DYNAMICS IN AQUEOUS SALT SOLUTIONS; A NMR CONTRIBUTION

J.R.C. VAN DER MAAREL, D. LANKHORST and J.C. LEYTE
Gorlaeus Laboratory, Dept. of Physical and Macromolecular Chemistry, P.O. Box 9502,
2300 RA Leiden, THE NETHERLANDS

^{2}H and ^{17}O relaxation rates were obtained for solutions of uni-univalent and bi-univalent salts in aqueous solutions and, in the ionic hydration layer, are linear functions of the electric field strength at the ionic surface; q/r^2.

To derive correlation times from the relaxation rates it is necessary to know the interaction, i.e. the ^{2}H and ^{17}O quadrupole coupling constants of the nuclei of the water molecules in the hydration layer. To this end the ^{17}O contribution to ^{1}H relaxation in ^{17}O enriched solutions was determined. [1] Apart from the small, and in this context negligible asymmetry parameter for ^{2}H, the correlation times for the ^{1}H-^{17}O dipolar interaction and the ^{2}H quadrupole interaction in water are equal. The ratio of the relaxation rates due to these contributions shows a small but significant change on comparing pure water and water in the hydration layer. In combination with a quantum relation of the bond length r_{OD} and the electric field gradient at ^{2}H, [2] our nmr results lead to a small correction of the quadrupole coupling constant of ^{2}H in the hydration layer. According to a correlation derived for crystal hydrates, some forms of ice and vapour, the same relative correction for ^{17}O is applied. [3]

Analysis of the ^{2}H and ^{17}O correlation times in terms of an axially-symmetric rotation diffusion model then leads to the following results for the structure-forming cations. If the main axis $D_{\parallel}$, of the diffusion tensor is taken to be located in the bisecting plane of the H_2O molecule, our results are consistent with an angle β between this main axis and the molecular plane of 0-30° in the limit $c \rightarrow 0$ which increases at higher concentrations. The ratio $D_{\parallel}/D_{\perp}$, does not exceed the value of 4 even for Mg^{2+}. Assuming that the $D_{\parallel}$ axis coincides with the axis connecting the cationic and oxygen nuclei, the preferred molecular orientation with respect to the cation from our results agrees with neutron diffraction data. [4,6]

For the anionic hydration layer such a simple connection of the direction of D and the orientation of the water molecule, with respect to the ion, is not possible. The direction of $D_{\parallel}$ is, however, poorly determined due to the small anisotropy in these cases.

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2-10(O) PROTON CHEMICAL SHIFTS OF HYDROGEN BOUND TO OXYGEN IN ALUMINIUM(III) COMPLEXES WITH MIXED WATER AND ALCOHOL LIGANDS

J.W. AKITT[1] and Helen ROBINSON[1] and Joel LELIEVRE[2]
[1]*The School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK and* [2]*Physicochimie des Solutions, ENSCP, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, 75321 Paris 05, FRANCE*

It is well known that first-sphere solvation numbers of the more highly charged cations can be obtained using proton nmr at temperatures low enough to reduce the solvent proton exchange rate sufficiently. [1] It has been found that, in moist alcoholic solutions of aluminium trichloride, the OH resonances on the oxygen bound to the cation in the various mixed species, $[Al(H_2O)_n(ROH)_{6-n}]^{3+}$ with $0<n<6$, can be observed at about -20 °C and are well resolved if a high enough magnetic field is used. [2] The resonances can be assigned to individual complexes by following the spectral changes which occur as the water content is increased. The OH chemical shifts span nearly 2 ppm, which is rather surprising for what are apparently similar entities, and vary irregularly with n, as alcohol is displaced by water. The electric field of the cation is believed to have the major influence on the chemical shifts of these protons but it is clear from these results that other, important, secondary influences are also present, and we will discuss the interactions of electric field, polarisation of the alkyl groups, penetration of anions within the alkyl groups of the first sphere and possible coordination of water and alcohol to the first sphere hydroxo protons.

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2-11(O) QUADRUPOLE RELAXATION OF IONIC NUCLEI AS A PROBE FOR LOCAL SYMMETRY AND SELECTIVE SOLVATION IN ELECTROLYTE SOLUTIONS

Manfred HOLZ[1] and Antonio SACCO[2]
[1] *Institut für Physikalische Chemie der Universität Karlsruhe, F.R.G.*
[2] *Dipartimento di Chimica, Università degli Studi, Bari, Italy*

Nuclear magnetic relaxation of ionic nuclei (e.g. $^{23}Na^+$ and $^{87}Rb^+$) which relax by the quadrupole-electric field gradient (QF) interaction, represents a shorter-ranged probe of an ion's neighbourhood than, for example, the ionic mobility. Thus this method is particularly well suited for solvent-solute interactions and is attracting increasing interest. [1,2] The quadrupole relaxation of ionic nuclei is influenced by dynamical and structural properties of the solvation shell. Thus the geometry and, in mixed-solvent systems, the composition of the first coordination sphere play an important role.

In spite of the fact that a proper theoretical evaluation of the absolute relaxation rates $1/T_1$ is rather difficult, we can develop techniques [3,4] which permit quantitative information about selective solvation of these monovalent ions and qualitative information about the local symmetry around these ions in pure and mixed solvent systems to be obtained.

These techniques are briefly outlined and we report on Na^+ and Rb^+ solvation in acetonitrile (AN), hexamethylphosphortriamide (HMPT), and aqueous mixtures of these two solvents. It can be shown that in the pure organic solvents the solvation shell is highly symmetric, and that in AN-H_2O mixtures these cations are preferentially hydrated, whereas in HMPT-H_2O the Na^+ ion is preferentially solvated by the organic solvent. [5]

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2-12(O) SODIUM CATION COMPLEXATION BY LARGE CROWN ETHERS IN LOW DONICITY SOLVENTS

Christian DETELLIER[1], Harald D.H. STOVER[1] and Alfred DELVILLE[2]
[1]*Ottawa-Carleton Chemistry Institute, University of Ottawa Campus, Ottawa (Ont.) CANADA K1N 9B4,* [2]*Institut de Chimie et de Biochimie, Université de Liège au Sart-Tilman, B-4000 Liege, BLEGIUM*

The complexation of sodium tetraphenylborate by the ligand dibenzo-24-crown-8 has been studied in nitromethane solutions by Na-23 nuclear magnetic resonance spectroscopy at three different fields. Chemical shifts, and transverse and longgitudinal relaxation measurements show the formation in solution of aggregates n + 1 : n sodium:crown.

Field-dependent transverse relaxation rates are affected by two relaxation mechanisms which can be separated: viz. quadrupolar and chemical exchange. This permits the precise definition of the kinetics parameter for sodium exchange between the solvated and the complexed states. At low sodium and crown concentrations ($<10^{-3}$ M), the exchange mechanism is a unimolecular decomplexation. At higher concentrations, the process obeys a bimolecular cation interchange mechanism whose kinetic parameters are $\Delta H^{\ddagger} = 27 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -120 \pm 10$ J K^{-1} mol^{-1}.

-13(0) SOLVATION EQUILIBRIA AND INTRAMOLECULAR DYNAMICS IN MIXED COMPLEXES OF NEUTRAL BIDENTATE ORGANOPHOSPHORUS LIGANDS AS STUDIED BY N.M.R.

T. CHNIBER, L. RODEHÜSER, P.R. RUBINI, and J.J. DELPUECH.
Laboratoire d'Etudes des Solutions Organiques et Colloidales (LESOC), UA CNRS No. 406 Université Nancy I, BP 239, F-54506 Vandoeuvre Cedex, FRANCE.

Neutral bidentate diphosphoramides of general formula $[(Me_2N)_2P(:O)]_2X$ proved to be very efficient complexing agents in non-aqueous media and excellent extractants from aqueous solutions for a wide variety of cations. In order to determine the relative stabilities of complexes containing different ligands, we studied the displacement of a weaker complexing agent, octamethylpyrophosphoramide (OMPA; X=O) by a stronger one, nonamethylimidodiphosphoramide (NIPA; X=N-CH_3), on complexes of the form $[M(NIPA)_i(OMPA)_{3-i}]^{n+}$ $(0<i<3$; M=Mg, Zn, Cd, In). Since the intermolecular ligand exchange is slow, separate signals are observed for the different complex species by ^{31}P n.m.r. The analysis of these spectra allows the determination of the equilibrium and formation constants characterizing the stepwise displacement reactions.

ML_3 (L=OMPA or NIPA) complexes show D_3 symmetry, and therefore all ^{31}P nuclei are magnetically equivalent. The introduction of a different ligand lowers the symmetry to C_2 so that coupling between the, now non-equivalent, phosphorus nuclei of the two other ligand molecules becomes apparent in the form of AB patterns. Intramolecular rearrangement, however, may be fast enough at higher temperatures to provoke coalescence of these signals.

From the analysis of line-shapes at different temperatures, kinetic parameters of the intramolecular motion in the mixed complexes could be determined and compared to those of the parent compounds studied earlier.

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2-14(O) STUDIES OF THE INTERACTION OF COBALT COMPLEXES WITH HYDROGEN BONDING SOLVENTS USING ^{59}Co NMR

D.R. EATON
Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, CANADA

Solvent-solute interactions affect both the chemical shifts and the relaxation times of the ^{59}Co nuclear resonances of coordination complexes in solution. The effects are particularly pronounced when second coordination sphere hydrogen bonding with the solvent can occur. Chemical shifts of more than 300 ppm between the same complexes in hydrogen bonding and non-hydrogen bonding solvents have been observed with the larger shifts being associated with the stronger hydrogen bonds. Data relating to ammine, cyano and nitro complexes will be presented.

The effects on the relaxation times are related to the lifetimes of the hydrogen bonds. In complexes of low symmetry there is a very large field dependence of both T1 and T2 in hydrogen bonding solvents which is not present in non-hydrogen bonding solvents. This is ascribed to relaxation due to chemical shift anisotropy modulated by the rapid formation and breaking of the hydrogen bonds. It is suggested that the off-diagonal (antisymmetric) components in the chemical shift tensor are responsible for this relaxation mechanism. T1 and T2 data for several complexes in different solvents will be presented to substantiate this conclusion.

Finally the relevance of the second coordination sphere lifetimes to the mechanisms of ligand exchange and catalytic reactions will be discussed.

2-15(C) STRUCTURE OF THIOCYANATO COMPLEXES OF ZINC(II), CADMIUM(II) AND MERCURY(II) IN AQUEOUS SOLUTION

Hitoshi OHTAKI, Kiyoshi YAMAMOTO and Toshio YAMAGUCHI
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 227 JAPAN

The structure of tetrathiocyanato complexes of Zn(II), Cd(II) and Hg(II) ions has been determined in aqueous solution by X-ray diffraction, Raman spectroscopy and ^{13}C and ^{14}N nmr measurements. The results indicated that nitrogen atoms coordinated to zinc(II) ion, while sulfur was the donor atom in the mercury(II) complex. On the other hand, in the cadmium(II) complex both nitrogen and sulfur atoms bound to the central metal ion. Structural data of the complexes are summarized in Table 1.

Table 1. Structural data of $[Zn(NCS)_4]^{2-}$, $[Cd(NCS)_2(SCN_2]^{2-}$ and $[Hg(SCN)_4]^{2-}$ complexes in aqueous solution at 25 °C.

	$[Zn(NCS)_4]^{2-}$	$[Cd(NCS)_2(SCN)_2]^{2-}$	$[Hg(SCN)_4]^{2-}$
r(M-N)/pm	204.1	224.6	-
r(M-S)/pm	-	264.9	253.5
r(M...N)/pm	-	435	415
r(M...S)/pm	462	487	-
M-N-S/deg	145	149	-
M-S-N/deg	-	106	102
ν(C-N)/cm^{-1} a)	2114	2105	2117
ν(C-S)/cm^{-1} b)	821	779(Cd-N) 732(Cd-S)	710
$\delta(^{13}C)$/ppm c)	1.4	-0.7	-4.9
$\delta(^{14}N)$/ppm d)	-30.3	-1.3	30.8

a) ν(C-N) of free NCS^- = 2068 cm^{-1}, b) ν(C-S) of free NCS^- = 747 cm^{-1}, c) Chemical shift of free NCS^- ($\delta(^{13}C)$ in water (135.0 ppm) is taken as the standard, d) Chemical shift of free NCS^- ($\delta(^{14}N)$ in water (185.3 cm^{-1}) is taken as the standard.

-16( ) THE STRUCTURE OF TIN(II) AQUA AND HALIDE COMPLEXES IN AQUEOUS SOLUTION BY MEANS OF EXAFS AND X-RAY DIFFRACTION

T. YAMAGUCHI,[1] O. LINDQVIST,[2] T. CLAESON[3] and J.B. BOYCE[4]
[1]*Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Yokohama 227, JAPAN*
[2]*Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, SWEDEN*
[3]*Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, SWEDEN*
[4]*Xerox Palo Alto Research Centre, Palo Alto, California 94304, U.S.A.*

EXAFS and X-ray diffraction techniques have been used to determine the structure of tin(II) aqua and halide complexes in aqueous solution and also to investigate the behaviour of Sn(II) lone-pairs in solution. The sample solutions measured were aqueous solutions of tin(II) perchlorate, and of tin(II) chloride and bromide with various X/Sn (X = Cl and Br) ratios from 1 to 8. In both perchlorate and halide solutions, it is found that the Sn(II) lone-pairs are stereochemically active and hence the Sn(II) environment consists of an Sn atom and three to four water molecules or halide ions bound to it with no molecule or ion at the lone-pair site. With increasing halide concentration, water molecules bound to Sn(II) are gradually replaced with halide ions and finally a trigonal pyramidal SnX_3^- species is formed even in solution containing a large amount of halide ions. These findings about Sn(II) halide complexes in solution are quite different from those in the crystalline state, in which the Sn(II) atom forms a regular octahedral SnX_6^{4-} in $CsSnX_3$ (X = Cl, Br and I) crystals with cubic unit cells. These results indicate that any distortion of coordination (the stereochemical activity of the Sn lone-pairs) gained from s-p mixing is easily suppressed by the external field such as packing forces.

[illegible] THE SOLVATED GOLD(I) ION IN PYRIDINE SOLUTION: A TETRAHEDRAL COMPLEX OF GOLD(I)

STEN AHRLAND, KARIN NILSSON, AKE OSKARSSON, INGMAR PERSSON and AKIO YUCHI

Inorganic Chemistry 1, Chemical Center, University of Lund,
P.O. Box 124, S-221 00 Lund, SWEDEN.

Copper(I) and silver(I) form tetrahedral solvates in pyridine solution, as evident from structure determinations by EXAFS, for copper(I) and by X-ray diffraction, for silver(I). From these solutions, the solvated ions can be crystallized as perchlorates; the metal-nitrogen distances are the same in the liquid and solid phases, viz. 2.05 Å for copper and 2.32 Å for silver.

The coordination of halide ions brings about a switch from the tetrahedral coordination to a linear one. This means an extensive desolvation where solvent molecules move from a well-ordered solvate into a not very ordered bulk solvent. Consequently the two steps necessary to form the linear dihalido complex are characterized by large gains of entropy.

The formation of dihalido complexes of gold(I) in pyridine has now been shown to involve similarly large gains of entropy. It is concluded that also gold(I) forms a tetrahedral solvate in pyridine. This seems to be the first regularly tetrahedral complex of gold(I) ever found.

Linear pyridine solvates of gold(I) have been found in solid halides of the stoichiometric composition AupyX, X = Cl, Br, I, which all contain the entities $Au(py)_2^+$ and AuX_2^-. In AupyBr, where these entities are well separated, the mean gold-nitrogen distance is 2.00 Å. In pyridine solution, however, the distance, as found by EXAFS, is 2.16 Å. A lengthening of the bond of this magnitude is just what to expect if gold(I) is tetrahedrally coordinated in the solution.

2-18(O) ON THE SOLVATION OF METHYLMERCURY(II) COMPOUNDS

Ingmar PERSSON[1] and Åke IVERFELDT[2]
[1]*Inorganic Chemistry 1, Chemical Center, P.O. Box 124, S-221 00 Lund, SWEDEN*
[2]*Department of Chemistry, Chalmers University of Technology, S-412 96 Göteborg, SWEDEN*

The solvation of some methylmercury(II) compounds in water and pyridine has been studied by means of calorimetry, Raman spectroscopy and large-angle X-ray scattering. The uncharged methylmercury(II) halides are stable compounds and higher complexes are not normally formed.

The heats of solvation of the methylmercury(II) halides are substantially less exothermic than those of the mercury(II) halides, irrespective of solvent used. The methylmercury(II) halides are much more weakly solvated than the mercury(II) halides, but much more strongly solvated than dimethylmercury.

The distribution of uncharged mercury species between the gas and the aqueous phases is given by the Henry's law constant, H, defined as $H = [HgX(g)][HgX(solv)]^{-1}$. The magnitude H is strongly correlated to the solvation of the mercury species. The Henry's law constants for some mercury species will be given.

We have found that methylmercury(II) hydroxide is hydrated only through hydrogen bonds to the hydroxide group and there are no water molecules coordinated to mercury. The methylmercury(II) hydroxide is linear in aqueous solution because of the lack of mercury-solvent bonds.

Raman spectroscopic studies have also shown that the methylmercury(II) halides are most probably linear in water as well as in other weakly donating solvents. These studies also showed that the methylmercury(II) halides are much more strongly solvated in pyridine. Pyridine is a sufficiently strong donor to solvate mercury in methylmercury(II) halides. Structural studies have shown two weak mercury-pyridine bonds and two additional pyridines at the sum of the van der Waal's distances from mercury.

2-19(O) A STUDY OF THE STRUCTURE OF WATER AND AQUEOUS SOLUTIONS, BASED ON THE ISOTOPE EFFECTS ON SOLVATION THERMODYNAMICS

Y. MARCUS and A. BEN-NAIM
Departments of Inorganic and Analytical Chemistry and of Physical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, ISRAEL

The solvation [1] of a particle in water, whether a "foreign" particle or a molecule of water, is expressed in terms of a non-hydrogen-bonding contribution to the pair potential and a contribution from hydrogen bonding. Only the latter depends on whether the water is H_2O or D_2O, since only the hydrogen bond energy differs between these kinds of water. [2] The effect of the isotopic constitution of the water on the solvation is examined for the cases of the dissolving particle being a water molecule and some solute. Estimates of the differences in the energies of the hydrogen bonds formed in H_2O, D_2O and T_2O are obtained from the enthalpies of sublimation of the respective ices. The average number of hydrogen bonds in which any water molecule in pure water participates is deduced from the Gibbs free energy and the enthalpy of condensation of molecules of the three kinds of water into the respective liquids. This number decreases from about 0.95 at 0 °C to about 0.35 at 100 °C, being a few per cent higher in D_2O than in H_2O. The Gibbs free energies of transfer of several kinds of solutes from light to heavy water are interpreted in terms of the average number of hydrogen bonds broken or made in the water per particle of solute. In the case of electrolyte solutes, division into the ionic contributions is made according to the tetraphenylarsonium tetraphenylborate assumption, using some new pertinent data. [3]

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-[illegible]) INTERACTIONS BETWEEN ALCOHOLIC OH GROUPS AND NON-POLAR SOLVENTS - A SPECTROSCOPIC STUDY

Werner A.P. LUCK, Thomas MENTEL and Stefan PEIL
Physikalische Chemie, Universität Marburg, Hans-Meerwein-Strasse,
D-3550 Marburg, F.D.R.

Recently we demonstrated a linear relationship between temperature and infrared frequency shift ($\Delta\nu$) for OH bands of several monomeric alcohols caused by non-polar van der Waals forces of different solvents. [1] The method of studying van der Waals forces by infrared frequency shifts was correlated with a simple liquid model. [2] Further experiments have established the validity of the linear dependence of the "red shift" upon temperature between 100 and 300 K. Matrix spectra in solid xenon have also confirmed the linear temperature dependence predicted by the model.

The measurements indicate that $\Delta\nu$ is proportional to the van der Waals attractions and, at higher densities, to the van der Waals repulsions. Using polychlorotrifluoroethane as solvent, we observed that $\Delta\nu$ has a minimum below 100 K and that ν even changed to higher frequencies (a "blue shift"). Similar measurements were made with a diamond cell at high pressures (up to 11 GPa). A "red-shift" is obtained at pressures below 1-2 GPa, but $\Delta\nu$ has a minimum at densities similar to those observed for temperatures for which $\Delta\nu = 0$ at 1 Pa, and $\Delta\nu$ decreases at higher pressures. With three different fluorinated alcohols in polychlorotrifluorethane at pressures close to 10 GPa we observed values of the frequency similar to values in the vapour phase and for 1,1,1,3,3,3,-hexafluoropropanol the solution phase frequencies were higher than the gas phase ones.

Our observations extend the infrared method used to study hydrogen bonding to an interesting method by which van der Waals interactions and their potential curves may be investigated.

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A-21(0) INTERACTIONS OF CATIONS WITH "SOFT" DONOR SOLVENTS

Gerhard GRITZNER
Johannes-Kepler-Universität Linz, A-4040 Linz, AUSTRIA

While numerous studies on ion-solvent interactions in "hard" donor solvents have been published, very few reports on "soft" donor solvents can be found in literature. Investigations in "soft" donor solvents such as N,N-dimethylthioformamide, N-methylthiopyrrolidone, hexamethylthiophosphoric triamide and 2-mercaptoethanol as well as in their "hard" analoga, N,N-dimethylformamide, N-methylpyrrolidone, hexamethylphosphoric triamide and ethanediol have been carried out using polarographic, voltammetric, spectroscopic, conductimetric and potentiometric methods to learn about the donor and, to some extent, about the acceptor properties of these solvents.

Gibbs free energies of transfer for the alkali metal ions, Tl^{+}, Zn^{2+}, Cd^{2+} and Ag^{+} have been chosen as these reflect the difference in interactions that "hard" and "soft" cations experience in soft solvents.

Based on these data, a classification scheme into "hard", "soft" and "borderline" solvents, as well as a semiquantitative order of "softness", will be proposed, since solvent parameters used at present cannot predict the interactions of "soft" cations with "soft" solvent molecules.

2-22(O) METAL COMPLEXES AS COLOUR INDICATORS FOR SOLVENT PARAMETERS

R.W. SOUKUP and R. SCHMID
Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 AUSTRIA

We present a simple method for assessing the coordination properties of solvents, solvent mixtures and solutes, which uses the solvatochromism observed in certain metal complexes.

The donor ability of a solvent is indicated by the colour of Cu(tmen) (acac)ClO_4, [1] where tmen = N,N,N',N'-tetramethylethylenediamine and acac = acetylacetonate. The wave number $\tilde{\nu}$(cm^{-1}) of the visible band and the solvent donor number (DN) are related empirically by the expression DN = 196 - 0.0102 $\tilde{\nu}$ for 12 solvents, including some at both ends of the solvent scale with a correlation coefficient of r of 0.99.

Similarly, the colour of a solution of $Fe(phen)_2(CN)_2$, where phen = 1,10-phenanthroline, indicates the acceptor power of the solvent. The acceptor numbers (AN) of 12 common solvents can be expressed as a function of the wave number of the long wavelength absorption of the complex [2,3] by the equation AN = -134 + 0.00933$\tilde{\nu}$; r = 0.98.

The colour changes of these two metal complexes in different solvents are so dramatic that, even with the naked eye, a rough ordering of acceptor and donor numbers is possible. These will be discussed in terms of simple ligand field theory.

The third important solvent parameter, dielectric constant, is reinterpreted in coordination chemical terms. [4]

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2-[illegible](C) RAMAN SPECTRAL STUDIES OF IRON(III) CHLORIDE SOLUTIONS

K. MURATA, D.E. IRISH, G.E. TOOGOOD
University of Waterloo, Department of Chemistry, Waterloo,
Ontario, N2L 3G1, CANADA

Iron(III) chlorides are important species in such systems as hot water loops of power generating stations because they contribute to the mechanism of corrosion. In this investigation a high temperature furnace assembly has been used to control the temperature of aqueous iron(III) chloride solutions to 300 °C at 9 MPa pressure. Raman bands characteristic of the complex at 25 °C (126, 158, 313 cm^{-1}) dramatically change as the temperature is raised. At 300 °C a sharp polarized band at 331 cm^{-1} and depolarized bands at 102 and 128 cm^{-1} occur. Interestingly, the spectrum of molten $FeCl_3.6H_2O$ at its melting point (37 °C) is identical with that of aqueous $FeCl_3$ solutions at 300 °C. Solutions of iron chloride, in non-aqueous solvents such as methanol and diethyl ether, show similar Raman spectra which are different from those of aqueous iron(III) chloride solutions. Results will be discussed in terms of the structural and co-ordination number changes which occur in aqueous and non-aqueous solutions as the temperature is raised.

2-24(O) PREFERENTIAL SOLVATION STUDIES OF SODIUM IODIDE IN ETHYLENEGLYCOL [EG] + ACETONITRILE [AN] AND IN PROPYLENE GLYCOL [PG] + ACETONITRILE [AN] MIXTURES

A.K. COVINGTON and M. DUNN
Department of Physical Chemistry, Bedson Building, University of Newcastle-upon-Tyne, Newcastle-upon-Tyne, NE1 7RU, U.K.

Studies on ion-solvent interactions in binary solvents consisting of protic and dipolar aprotic components are receiving increasing attention. The drastic change in the solvating medium upon the addition of a protic solvent to a dipolar aprotic solvent obviously affects the nature of ion-solvent interactions, and hence ionic solvation. Changes in ionic solvation have important consequences in such diverse areas as the rates of base-catalysed reactions, and organic syntheses. ^{23}Na nmr chemical shifts, and I^- CTTS band maxima have been used as probes for ion-ion and ion-solvent interactions for NaI in EG + AN and PG + AN. Since EG + AN form approximately isodielectric mixtures, changes in ion-solvent interactions on transfer from the pure solvents to EG + AN mixtures can be attributed to changes in the short range 'chemical' interactions. Solute-ion nmr studies and UV band maxima are especially suited as probes for these short range ion-solvent interactions and the composition of the solute solvation shell. In combination with a stepwise thermodynamic model for solvation in a binary solvent taking into account non-ideal solvent behaviour, such studies can provide quantitative evidence for preferential solvation. For both systems, preferential solvation by the glycol was detected.

3-1 (O) A STUDY OF HYDROGEN-BONDED SPECIES OF ACETIC ACID IN WATER

Salag DHABANANDANA, Pipat KARNTIANG and Vitaya RUANGPORNVISUTI
Faculty of Science, Chulalongkorn University, THAILAND

Hydrogen-bonded species, viz monomers, linear dimers, cyclic dimers, polymers and free ions existing in an aqueous solution of acetic acid, were quantitatively determined at 32 °C in the concentration range of 0-100 %w/w. The amount of each hydrogen-bonded species present for some ranges of concentration was determined from three equilibrium constants namely, the equilibrium constant of formation of (i) the cyclic dimer from two monomeric acid units (K_c), (ii) a linear dimer from two monomeric acid units (K_1), and (iii) a polymer of i+1 units from a monomer unit added to i units of polymer (K).

The three equilibrium constants were obtained by a non-linear least-squares fit of the observed proton chemical shifts. [1] These values of K, K_1 and K_c are to 54.4 mf^{-1}, 141.7 mf^{-1} and 262.5 mf^{-1} respectively and are statistically acceptable in the concentration range 0-85 %w/w.

The predominant species were respectively as follows; monomer, cyclic dimer, cyclic dimer and linear dimer, and polymeric species at (1.6-8.0) x 10^{-3} %w/w,(6.0-20.0) %w/w, (10.0-25.0) %w/w and (50.0-85.0) %w/w.

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3-2 (O) SOLUTE-SOLVENT AND SOLVENT-SOLVENT INTERACTION PARAMETERS FOR INFINITELY DILUTE SOLUTIONS OF HALOALKANES IN SQUALANE-DINONYL PHTHALATE MIXTURES: EVIDENCE FOR WEAK 1:1 HALOALKANE:DINONYL PHTHALATE COMPLEXES

G. A. OWEIMREEN

Department of Chemistry, University of Petroleum and Minerals,
Dhahran 31261, SAUDI ARABIA.

Using gas liquid chromatography, infinite dilution activity and partition coefficients were obtained at 30.00 °C for six haloalkane solutes in pure squalane (SQ), in pure dinonyl phthalate (DNP) and in five mixtures thereof. The solute partition coefficients in the solvent mixture differed by as much as 10% at $\phi_{DNP} = 0.453$ ($x_{DNP} = 0.500$) from those calculated from the partition coefficients in the pure single solvents using the Purnell-Andrade equation [1]. The results from this and other [2-4] systems show that, in general, the Purnell-Andrade equation may not accurately predict data for solvent mixtures, especially when the volume fractions of the solvent components are comparable.

On the other hand, theoretical expressions derived by Harbison et al. [4] on the basis of conventional models of solution, fitted the data to within experimental error (1.2%), and were used to calculate solute-solvent and solvent-solvent interaction parameters. The solute-solvent interaction parameters indicate the existence of weak 1:1 complexes between each of the haloalkane solutes and DNP. The association constants of these complexes were evaluated and qualitatively rationalized on the basis of the structures of the haloalkane molecules.

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3-3 (O) ON THE ACIDITY FUNCTION H_0 AND SOLVENT COMPOSITION

H. SADEK
University of Alexandria Research Centre [UNARC], P.O. Box 832, Alexandria, EGYPT.

The maximum value of the acidity function, H_0, usually observed in water-organic solvent systems for a given acid concentration has been analysed. Two proton transfer equilibria are proposed. In water-rich solvent mixtures, the equilibrium A : $H_3O^+ + S \rightleftharpoons HS^+ + H_2O$ applies successfully to water-methylcellusolve (MCS) over a wide range of acid concentration up to 40 wt% MCS. Equilibrium A was also found to apply to water+EtOH and water+acetonitrile (AN). Plots of H_0 + log [HCl] against the solvent composition ratio $[S]/[H_2O]$ were straight lines in all cases with slope equal to $K_1'/2.3$. The values of the equilibrium constant K_1' were 10.45, 9.47 and 9.7 for H_2O + MCS, H_2O + EtOH and H_2O + AN solvent systems, respectively. The main assumption is that $H_0 = \log[H_3O^+] - \log F_I$, where $F_I = (\gamma_{H^+}/\gamma_{BH^+})\,\gamma_B$ and B is the indicator base, p-nitroaniline. In organic solvent-rich systems (>60 wt% S), the proton transfer equilibrium B : $HS^+ + H_2O \rightleftharpoons H_3O^+S$ is also applicable. The values of the equilibrium constant K_2' were 0.324 and 0.455 for MCS + H_2O and AN + H_2O, respectively. With known values of K_1' and K_2', it was possible to calculate $[H_3O^+]$ and $[HS^+]$ in any solvent system. $[H_3O^+]$ decreases rapidly as the MCS content increases to 40 wt%; between 40 and 60 wt% $[H_3O^+]$ remains almost unchanged, but on further increase of MCS content, $[H_3O^+]$ decreases again. $[HS^+]$ behaves in an analogous manner but changes in the opposite direction. The main assumption in these calculations is $[HCl] = [H_3O^+] + [HS^+]$ in any medium. It was also possible to show that the change of $-\log F_1$ with solvent composition is an S-shaped plot, with major changes in the middle range of solvent composition.

3-4 (O) SPECTROSCOPIC AND CONDUCTANCE EVIDENCE FOR SOLUTE-SOLUTE INTERACTIONS IN PHENOL AND BUTENONE DERIVATIVES.

O.DABBIT, S. EL KADRY and S. WASIF
Department of Chemistry, Faculty of Science, Aleppo University,
Aleppo, SYRIA

Spectroscopic and conductometric studies of weak acids (phenol and butenone derivatives) agree on the behaviour of such acids in different nonaqueous media.

Using UV/V and IR spectra, it was possible to differentiate between ionisation and association of such acids. Their interactions with amines point to their differential behaviour which ranges from full ionisation of the stronger derivates to association of the weaker ones.

Conductance measurements could be used, along with spectroscopic techniques to evaluate their ionisation constants, pK_a, in different solvents. Ion pair formation is suspected to exist in varying degrees in different solvents.

[illegible]-5 (O) STUDIES ON DISSOCIATION CONSTANTS AND ION-SOLVATION IN AQUEOUS EHTANOL, NON-AQUEOUS SOLVENTS AND THEIR AQUEOUS MIXTURES OF SOME BENZOCYCLOBUTEN-1(2H)ONES

Saad WASIF, Barsoum NASHID and George M. ISKANDER
Department of Chemistry, University of Khartoum, Khartoum, SUDAN

The pK_a' values of five 4-hydroxybenzocyclobuten-1(2H)ones (I) in aqueous ethanol, dioxane, acetonitrile and dimethylformamide have been determined. The Hammett parameter, σ, varies for each phenolic ketone with the aqueous solvent composition, which reflects possible sensitivity to solvent polarity. The molar free energies of transfer of (I) from water to 20-60 wt % of organic solvent-water mixtures have been evaluated. The results so obtained, are explained by a structural theory of ion solvation.

3-6 (O) THERMODYNAMICS OF TRANSFER OF TRIS-(HYDROXYMETHYL)-AMINOMETHANE AND P-NITROANILINE INDICATOR FROM WATER TO AQUEOUS -2-METHOXYETHANOL MIXTURES. SOLVENT EFFECT ON THE DISSOCIATION OF THEIR PROTONATED BASES

A.A. EL-HARAKANY and A.O. BARAKAT
Chemistry Department, Faculty of Science, Alexandria University, Alexandria, EGYPT

Despite the fact that 2-methyoxyethanol (MCS) has been found to be an excellent solvent for a variety of organic and inorganic compounds, its solvent structure and solvent effect on the dissociation of BH^+ type acids is still incompletely understood.

In this work both p-nitroaniline and tris-(hydroxymethyl)-aminomethane are used as a solvent-structure probe. Their solubilities at 20, 25, 30, 35, and 40 °C in H_2O + MCS solvents containing 0 - 100% MCS have been determined. The standard thermodynamic functions of transfer for the dissolution process in the various mixtures have been derived from the variation of the solubility with temperature. An attempt has also been made to interpret the patterns of solute-solvent interactions in terms of the free energies of transfer of the base and its protonated form.

Comparison of the data obtained for the non-electrostatic part of the free energy of transfer $\Delta G^{\ominus}_{t,ch}$ from H_2O to H_2O + MCS mixtures for p-NAH^+, tris-H^+, and H^+ shows that the more negative values of $\Delta G^{\ominus}_{t,ch}$ for p-NAH^+ as compared with tris-H^+ may imply that the hydrophobic effect of the aromatic nucleus outweighs any specific solvation involving the three terminal hydroxy groups in the tris-H^+.

3-7 ([illegible]) FIRST DETERMINATIONS OF STABILITY CONSTANTS IN LIQUID AMMONIA SOLUTIONS USING POTENTIOMETRIC TITRATIONS: CYANO- AND THIOCYANATO-SILVER(I) COMPLEXES AT 233 K

Yvonne M. CHEEK, Peter GANS and J. Bernard GILL
Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, U.K.

Previously we studied the complexation of Ag^+ by CN^- and NCS^- in liquid ammonia by Raman spectroscopy. At least 11 species participate in the equilibria between complexes formed from Ag^+ and CN^-. With NCS^- only a weak 1:1 complex forms and a large excess of $[NCS^-]_T$ is required to form $[Ag(NCS)_2]^-$ at low concentration. [1,2]

We now report an extension of the spectroscopic studies of these systems (which provided only qualitative information about the equilibria of complexation) to a quantitative examination by potentiometric titrations of Ag^+ with both CN^- and NCS^-. A concentration cell was used to follow the titrations. At $[Ag^+]_T \sim 10^{-4}$ to 10^{-3} mol dm^{-3} only complexes of 1:1 and 1:2 stoichiometry are discernable in the Ag^+/CN^- titrations. However, from the fitting of calculated stability constants to the observed data, using the new SUPERQUAD program, a third 1:3 step seems likely: $\log K_1 = 7.0$, $\log K_2 = 9.1$ and $\log K_3 = 1.5$ (mol dm^{-3} units). A small change in cell e.m.f. of only 5 mV during the titration of Ag^+ by SCN^- indicates a very low formation constant for AgNCS of $K_1 \sim 5$ mol^{-1} dm^3.

The results are consistent with our spectroscopic observations.

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3-8 (O) SOLUTION AND PROTONATION OF PURINES AND RELATED BASES IN DIMETHYLSULFOXIDE

R.L. BENOIT and M. FRÉCHETTE
Dept. of Chemistry, Université de Montréal, C.P. 6128, Succ. A,
Montréal, Québec, CANADA, H3C 3V1

Since purines are important constituents of nucleic acids, the thermodynamics of the first protonation steps of purines in aqueous media is well documented. However, there are few corresponding data on these reactions in dimethylsulfoxide despite the wide use of this solvent in studies on purines and nucleic acids. We have therefore studied the thermodynamics of the solution and protonation of purines and related bases in Me_2SO.

We determined potentiometrically the ionization constants, K, of the conjugated acids BH^+ of purine, adenine, 9-methyladenine, adenosine, guanine, and hypoxanthine, and of the related bases, imidazole, N-methylimidazole, benzimidazole, and 4-amino-2,6-dimethylpyrimidine. We also obtained the heats of solution and the heats of protonation of most of these bases calorimetrically. While the pK values show generally minor decreases when passing from water to Me_2SO, the enthalpy values are definitely more exothermic in Me_2SO. Our discussion of the solvent effect on these data is based on a consideration of the enthalpies of transfer of B and BH^+ and emphasizes the contrasting H-bonding properties of the solvents and of the functional groups on the B and BH^+ solutes. Available gas phase data and results of theoretical calculations are evaluated in the light of our Me_2SO data.

3-9 (O) THERMODYNAMICS IN NON-AQUEOUS SOLVENTS. URANYL(VI) COMPLEXES WITH AMINES IN DIMETHYL SULFOXIDE

A. CASSOL[a], P. DI BERNARDO[a], R. PORTANOVA[b], M. TOLAZZI[b], G. TOMAT[a] and P. ZANONATO[a]
[a]*Istituto di Chimica, Università di Padova, Via Loredan 4, 35100, Padova, ITALY,* [b]*Istituto di Chimica, Università di Udine, Viale Ungheria 43, 33100 Udine, ITALY*

Over the past years, a number of papers has been published on the thermodynamics of uranyl(VI) complex formation in aqueous solution. [1] In water, the uranyl(VI) ion displays a typically "class a" or "hard" behaviour with a strong preference for oxygen donor ligands. In aqueous solution some equilibrium studies cannot be carried out on account of the protolytic equilibria of the uranyl(VI) ion, which occur in moderately acidic solutions. This is the case for ligands coordinating through nitrogen such as amines which are, in fact, protonated in the pH region where the hydrolysis of the uranyl(VI) ion is negligible. In order to get information about such systems, an aprotic solvent, e.g. DMSO, is chosen. *In this investigation, the thermodynamic functions for the complex formation* of the uranyl(VI) ion with a number of ligands, all coordinating via nitrogen, and ranging from simple mono-amines to polyamines, are reported. The investigation has been carried out at 25 °C and in a medium of ionic strength 0.1 M with Et_4NClO_4. The stability constants of the uranium(VI) complexes have been obtained by potentiometric measurements using the method of competitive complex formation with, silver(I) as the auxiliary central group. The enthalpy changes for the uranium(VI) complexes, as well as those for the silver(I) complexes, have been obtained by direct calorimetric measurements. The uranium(VI) and silver(I) complexes with amines are all enthalpy-stabilized, whereas the entropy contributions counteract the complex formation quite strongly. The low stability of the uranium(VI) complexes, compared with the analogous silver(I) complexes, reflects the stronger solvation of UO_2^{2+} in DMSO, which is also confirmed by less favourable enthalpy contributions, and more favourable entropy contributions, to the stability of the uranium(VI) complexes.

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3-10(O) SOLVATION AND SLOW SOLVENT EXCHANGE PROCESSES ON SIX-COORDINATE LANTHANIDES. A KINETIC AND MECHANISTIC STUDY.

Stephen F. LINCOLN and Alex WHITE
Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001, AUSTRALIA

In water the trivalent lanthanides (Ln^{3+}) are either reported to be all nine coordinate [1] or to exhibit a progressive decrease in coordination number from nine to eight with the lanthanide contraction. [2] In N,N-dimethylformamide (dmf) solution the coordination number changes from nine to eight with the lanthanide contraction, [3] and our studies show that in 1,1,3,3-tetramethylurea (tmu) solution the heavy lanthanides are six-coordinate. The lability of coordinated solvent decreases in the sequence: $[Ln(OH_2)_9]^{3+} > [Ln(dmf)_8]^{3+} > [Ln(tmu)_6]^{3+}$ by several orders of magnitude. The change in coordination number and lability appears to correlate closely with the size of the solvent molecule. These correlations will be discussed in conjunction with our new data on $[Ln(tmu)_6]^{3+}$ where Ln = Ho, Er, Tm and Yb which shows tmu exchange to be remarkably slow ($k(298\ K) = 60\ s^{-1}$ for Yb) and our recently published data for Ln = Lu. [4]

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3-11(O) COMPLEX FORMATION OF BIVALENT METAL ION WITH MONOAMINOMONOCARBOXYLIC ACIDS

Haruo MATSUI
Government Industrial Research Institute, Nagoya, 1, 1-chome,
Hirate-Cho, Kita-ku, Nagoya, 462 JAPAN

It is well known [1] that, in complex formation of a metal ion with analogous ligands, the stability of the complex increases with the increase in basicity of the ligand. However, when we compare the stability constants of glycine complexes with some bivalent metal ions, such as cobalt(II), nickel(II),copper(II), zinc(II), and cadmium(II), with those of α-alanine complexes, the former have somewhat larger values than the latter despite the fact that α-alanine has larger basicity than glycine. One reason for such contradiction is that methyl substitution brings about steric hindrance for α-alanine complexes with the metal ions. However, from the results of experiments on mixed ligand cadmium(II) complexes (CdLL'), which consisted of a glycine and a methylene-substituted α-aminocarboxylic acid, it was indicated that monoglycinatocadmium(II) complex(CdL^+, L^- = glycinate anion) was more strongly coordinated with the methylene-substituted α-aminocarboxylate anion(L'^-) than with glycinate anion [2]. These results suggest that there will be not only steric but also other factors involved in complex formation of glycine or α-alanine with bivalent metal ions. Complex formation of cadmium(II) ions with monoaminomonocarboxylic acids such as glycine, α-alanine, β-alanine, 2-aminobutanoic acid, 3-aminobutanoic acid, 4-aminobutanoic acid, 2-aminopentanoic acid, 5-aminopentanoic acid, 2-aminohexanoic acid, and 6-aminohexanoic acid was investigated in aqueous solutions containing 3 mol dm^{-3} $LiClO_4$, as a constant ionic medium, at 25 °C by potentiometric titration. The relationship between stability constant of the complex and basicity of ligand will be discussed from the results obtained in studies of cadmium(II)-monoaminomonocarboxylic acids and cadmium(II)-other ligands, which have an analogous structure to glycine or α-alanine, such as α-hydroxycarboxylic acids and α-mercaptocarboxylic acids.

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3-12(O) EFFECT OF SOLVENT POLARITY AND OF SUBSTITUENTS ON EQUILIBRIA IN THE SYSTEMS: Me(II) - TU - SOLVENT

Joanna MASLOWSKA and Krystyna WOJTYSIAK
Institute of General Food Chemistry, Technical University of Łódź, ul. B. Stefanowskiego 4/10, 90-924 Łódź, POLAND

Thiourea (TU) and its numerous derivatives have found applications in pharmacy and medicine due to their specific properties. The aim of our studies has been to find the effect of solvent on equilibria in the systems: TU - Solvent or Me(II) - TU - Solvent. The following reagents were used: thiourea, 1-methylthiourea, 1-ethylthiourea, 1-butylthiourea, 1,3-dimethylthiourea and 1,3-diethylthiourea. As organic solvents, the following were used: dimethylsulphoxide (DMSO), dimethylformamide (DMF) and acetonitrile (AN).

It has been shown by means of polarographic and potentiometric methods that, in polar aprotic donor solvents such as DMF or DMSO, complexes of Pb(II) and Cd(II) with TU and their derivatives of the type: $[Pb(Solv)_n(L)_j]^{2+}$ $(j + n = 4)$ are formed. The stabilities of complexes formed in organic solvents are affected by variation of the reaction enthalpy change which becomes more positive as the coordinated solvent molecule is replaced by ligand of lower basicity. The relationships so obtained:

$$\log \beta_j = f(1/DN) \quad \text{and} \quad \log \beta_j = f(\Sigma\sigma^*)$$

(where DN is the donor number of Gutmann [1] and σ^* is the sum of the polar effects of substituents R in thiourea [2,3] enabled the effects of both of the substituents and the medium on the stability of the complexes to be investigated.

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3-13(O) REACTTION OF ETHYL IODIDE WITH BROMIDE ION. REACTION RATES AND TRANSFER ENTHALPIES OF ANIONS IN N-METHYLACETAMIDE + ACETONITRILE AND N-METHYLACETAMIDE + N,N-DIMETHYLACETAMIDE MIXTURES.

Yasuhiko KONDO, Akikazu NAKANO, and Shigekazu KUSABAYASHI
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, JAPAN.

Recently, there has been much interest in N-methylamides as solvating media, because of their capabilities of exerting protic, as well as dipolar aprotic, interactions towards ions, as well as their high permittivities. In the attempts to characterize solute-solvent interactions in N-methylacetamide, we have measured the rates and activation parameters for bromide ion-ethyl iodide reaction, and the enthalpies of solution for tetra-butylammonium bromide, tetra-butylammonium perchlorate, and ethyl iodide in N-methylacetamide + acetonitrile and N-methylacetamide + N,N-dimethylacetamide mixtures.

Single ion transfer enthalpies have been determined on the tetra-butylammonium / tetra-butylborate ion assumption, and are summarized in Table 1. (acetonitrile is chosen as standard solvent).

Table 1. $\Delta H_t^{AN \to S}$ / kJ mol^{-1}

Ions	Methanol	NMA	DMA	NMePy
BBu_4^-	-5.0	-4.3	-11.3	-12.6
ClO_4^-	22.6	21.4	4.3	6.7
Br^-	5.7	10.9	10.7	16.8

AN, Acetonitrile; NMA, N-Methylacetamide; DMA, N,N-Dimethylacetamide; NMePy, N-Methylpyrrolidone.

With respect to anion solvation, N-methylacetamide behaves just like methanol, and there is a clear distinction between the dipolar aprotic solvents, i.e., DMA and NMePy, and the protic solvents, i.e., MeOH and NMA. Further discussion will be given on a more detailed analysis of bromide ion and transition state anion solvation in these solvent mixtures.

-14(O) EFFECT OF CARBON TETRACHLORIDE AND AROMATIC CO-SOLVENTS ON THE METHANOLYSIS OF t-ALKYL HALIDES

C.A.N. VIANA*, M.L.S. LOPES*, B.J. HEROLD**, M.R.Q. GODINHO**
**Centro de Electroquimica e Cinética da Universidade de Lisboa,*
Faculdade de Ciencias, 1294 Lisboa Codex, PORTUGAL
***Centro de Processos Químicos da Universidade Técnica de Lisboa,*
Instituto Superior Técnico, 1096 Lisboa Codex, PORTUGAL.

In order to explain the observed rate enhancement in the methanolysis of saturated tertiary halides caused by presence of aromatic co-solvents and carbon tetrachloride, previously reported by us [1,2] we have continued with kinetic and thermodynamic studies, as well as with the study of several properties of the binary solvent mixtures involved.

We present the kinetic and thermodynamic results of methanolysis of 2-chloro-2-methylpropane, 3-chloro-3-ethylpentane and 1-bromoadamantane in the presence of p-xylene and of CCl_4, at different temperatures, confirming the catalytic effect of these co-solvents.

We also present surface tension results for the binary mixtures methanol + p-xylene and methanol + carbon tetrachloride, showing no self-micellisation, as well as the results of NMR and $E_T(30)$ and Y parameter studies, showing the existence of critical transition concentrations in the behaviour of these solvent mixtures.

All these studies point to a specific co-solvent-solvent interaction as principal cause for the observed effect, and show that the rate enhancement is mainly dependent on preferential solvation of the transition state, which preceeds the ion-pair, by methanol.

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3-16(O) THE NEUTRAL HYDROLYSIS OF TWO 1-ACYL-1,2,4-TRIAZOLES IN BINARY AQUEOUS MIXTURES: ISOBARIC VERSUS ISOCHORIC ACTIVATION PARAMETERS

Jan R. HAAK[1], Jan B.F.N. ENGBERTS[1] and Michael J. BLANDAMER[2]

[1]*Department of Organic Chemistry, University of Groningen,*
Nijenborgh 16, 9747 AG Groningen, THE NETHERLANDS

[2]*Department of Chemistry, University of Leicester, Leicester*
LE1 7RH, ENGLAND

Kinetic solvent effects are usually analyzed in terms of the transition-state theory. In this approach, the temperature-dependence of the rate constants at constant pressure gives an enthalpy of activation. Trends in this parameter as a function of solvent (composition) can be explained in terms of changes in solute-solvent interactions. [1] Already in 1935 Evans and Polanyi [2] raised the question whether it would not be more suitable to analyze the temperature-dependence at constant volume in order to eliminate the temperature-dependence of solute-solvent interactions. This idea was further examined by Whalley and co-workers [3] in the nineteen sixties. The present paper gives a detailed consideration of the Evans and Polanyi proposal. This is illustrated by the isobaric-isochoric conversion for the activation parameters for the neutral hydrolysis of a hydrophilic and a hydrophobic substrate. These results and other considerations reveal that constant volume is not a sufficient constraint for temperature-independent solute-solvent interactions. [4]

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3-17(O) THE SOLUBILIZATION OF ORGANIC SOLUTES BY AQUEOUS MICELLAR SOLUTIONS

Sherril D. Christian[1], Edwin E. TUCKER[1], and John F. SCAMEHORN[2]
Department of Chemistry[1] and School of Chemical Engineering and Materials Science[2], the University of Oklahoma, Norman, OK 73019, U.S.A.

We are studying the solubilization of organic solutes in surfactant micelles with vapour pressure and dialysis methods. High-precision solute vapour pressure isotherms are obtained for aqueous systems of accurately known composition, varying from infinite dilution nearly to saturation. A new method called semi-equilibrium dialysis (SED) is used to obtain solubilization constants for nonvolatile solutes in micellar solutions.

In the SED experiments, a solution of surfactant and organic solute is placed on one side of an equilibrium dialysis cell and pure water is placed on the other side. After 18 to 24 h the concentrations of surfactant and organic solute in the dilute solution compartment are determined. Even when quite concentrated surfactant solutions are used, the concentration of surfactant in the dilute solution compartment (after 18 to 24 h) only slightly exceeds the critical micelle concentration. Experiments with dilute binary aqueous solutions show that monomers of the surfactant and the organic solute transfer through the membrane with half-lives of about 2 h. Therefore, we conclude that in the SED experiments with concentrated mixtures of surfactant and organic solute, the organic solute reaches equilibrium with respect to the solutions on both sides of the membrane. The surfactant, on the other hand, continues to transfer very slowly through the membrane so long as a difference in concentration exists between the solutions in the two compartments. Solubilization equilibrium constants can be inferred directly from the known concentrations of the components in both compartments of the SED cell.

Data are presented for solutions of n-hexadecylpyridinium chloride and one or more of the solutes: benzene, n-hexane, phenol, tert-butylphenol, o- and p-cresol, and several normal aliphatic alcohols. A mass action model is used to interpret the extensive deviation from Henry's law exhibited by the solubilization isotherms.

THEME 4

Transport properties of fluids (conductivity, viscosity, diffusion etc.)

ORAL CONTRIBUTIONS

4-1(0) TEMPERATURE DEPENDENCE OF ION ASSOCIATION OF $[Co(gly)(en)_2]^{2+}$ WITH SULFATE AND OXALATE IONS IN WATER

Haruhiko YOKOYAMA and Kiyoshi YAMAMOTO*

*Department of Chemistry, Yokohama City University, Kanazawa-ku, Yokohama, 236 JAPAN and *Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Midori-ku, Yokohama, 227, JAPAN*

The electric conductivities of aqueous solutions of bis(ethylenediamine)glycinatocobalt(III) sulfate and oxalate have been measured at various temperatures from 0 to 50°C and analyzed to obtain the ion-association constant K by using the expanded Fuoss-Hsia equation[1] on the assumption of a=6 Å.

The derived values of K and $\Lambda^{\infty}(\frac{1}{2}[Co(gly)(en)_2]X)$ are given in Table 1. As shown in Fig. 1, the K values of the complex salts are considerably larger than those obtained for $MgSO_4$[2] and those predicted from the ion-association theories[3,4], and have minima at characteristic temperatures t_m. The latter phenomenon is of interest in connection with the temperature dependence of the acid dissociation constant[5]. The results imply that exothermic short-range interactions, independent of the dielectric constant of the medium, exist between $[Co(gly)(en)_2]^{2+}$ and the anions.

Table 1. K/dm^3mol^{-1} and $\Lambda^{\infty}/S\ cm^2mol^{-1}$

	$[Co(gly)(en)_2]SO_4$		$[Co(gly)(en)_2]C_2O_4$	
t/°C	K	Λ^{∞}	K	Λ^{∞}
0	325±6	66.30±0.08	165±2	62.79±0.04
5	318±6	77.66±0.09	164±2	73.80±0.05
10	312±5	89.67±0.10	165±2	85.47±0.05
15	310±5	102.24±0.11	166±2	97.71±0.06
20	309±5	115.34±0.11	168±2	110.51±0.07
25	311±5	128.99±0.12	170±2	123.81±0.07
30	313±5	143.10±0.13	173±2	137.59±0.08
35	318±5	157.68±0.14	177±2	151.80±0.09
40	324±5	172.64±0.15	182±2	166.42±0.10
45	332±5	188.05±0.18	187±2	181.44±0.12
50	341±5	203.82±0.21	193±2	196.83±0.12

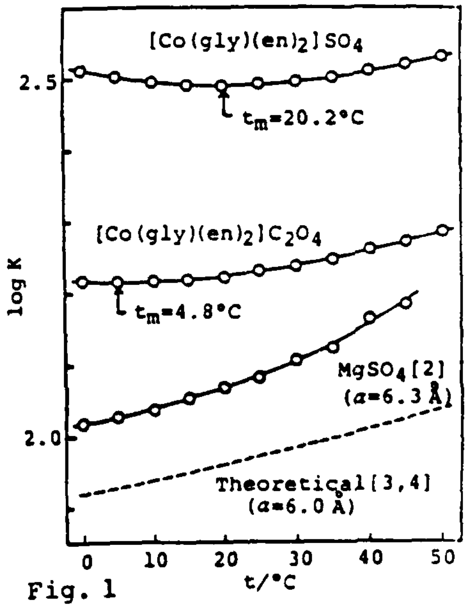

Fig. 1

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4-2 (O) POSSIBLE DIMERIZATION OF SOME SUBSTITUTED BENZOIC ACIDS

Laurence E. STRONG[1], Robert RYTHER[1] and Alan D. PETHYBRIDGE[2]

[1] *Chemistry Department, Earlham College, Richmond IN 47374 U.S.A.*

[2] *Chemistry Department, University of Reading, Reading, RG6 2AD, ENGLAND*

Conductance measurements have been made on aqueous solutions of benzoic, 2-methylbenzoic and 2,6-dimethylbenzoic acids up to concentrations close to saturation and at temperature from 5° to 100 °C. When the data were fitted to a conductance equation such as the one developed by Fuoss in 1978 it was found that above about 5 millimolar the molar conductance was less than what was calculated by the theory and the discrepancy was larger the higher the concentration. Solubility of about 0.028 M for benzoic acid at 25 °C imposes a limit on the high concentration end. On the assumption that the deviations were the result of the acid dimerizing, calculations of the dimerization constant $K_D = [(HBZ)_2]/[HBZ]^2$ were made. At 25 °C the constants were 1.6, 1.8, and 1.1 for benzoic, 2-methylbenzoic and 2,6-dimethylbenzoic acids, respectively. For the first two acids K_D decreases with rise in temperature while it increases for 2,6-dimethylbenzoic acid. Dimerization has been claimed for acetic acid on the basis of conductance data that did not fit conductance theory for a 1-1 electrolyte. However, the concentration at which the deviation becomes significant is high enough that questions have been raised about the validity of the dimerization explanation. In contrast to the estimated dimerization constant for acetic acid of about 0.1 at 25 °C, the benzoic acids that have been studied thus far have constants more than 10 times larger and the deviations are significant at concentrations below 0.02 M.

4-3 (O) PROPERTIES OF SELECTED NON-AQUEOUS $LiClO_4$ SOLUTIONS FROM CONDUCTANCE MEASUREMENTS AND FUOSS EQUATION ANALYSES

L. WERBLAN, A. SUZDORF, J. LESIŃSKI, G. SZYMAŃSKI
Department of Chemistry, The University of Warsaw, 1 Pasteura St., 02-093 Warsaw, POLAND

This research has focussed on the ion transport mechanism in solvents of low and medium dielectric constant. Electrical conductances have been determined for lithium perchlorate solutions in two-component mixtures of γ-butyrolactone with ethers (1,1-dimethoxyethane, 1,2-dimethoxyethane and tetrahydrofuran) over concentration ranges from 10^{-6} mol dm^{-3} to near saturation. The results obtained for dilute solutions have been analysed numerically with the Fuoss equations. [1] The dissociation constants of ion-pairs and dissociation constants of ion-triplets, the limiting conductances at infinite dilution, and the parameters of closest approach for the ion-pairs and triple ions have been calculated. The values of these parameters have been critically analysed.

From conductance measurements at medium and high concentrations of electrolyte, the compositions of the solutions with the maximum specific conductivity have been determined and are discussed from the point of view of lithium battery development. [2,3]

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4-4 (O) THE FIRST IONIZATION CONSTANT OF ORTHOPHOSPHORIC ACID TO 250 °C AND TO 2000 BAR

Allan J. READ
Chemistry Division, DSIR, Private Bag, Petone, NEW ZEALAND

Conductivity measurements can provide useful information on the ionization behaviour of weak acids over a range of conditions. The conductivity cell used to high temperatures and pressures is constructed from inert materials and includes a flexible gold bag to accommodate volume changes with varying pressure and temperature. Pressure coefficients of conductivity for KCl solutions determined in the cell are in excellent agreement with the best literature data.

The cell has been used to investigate the ionization (1) from

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad (1)$$

25 to 250 °C and to 2000 bar. K_1 decreases over this temperature interval and $\Delta\bar{V}^\circ$ becomes increasingly negative over the same range. Thermodynamic data for the first ionization of orthophosphoric acid are compared with results obtained by other techniques.

4-5 (O) SOLVENT ISOTOPE EFFECT ON MOBILITY OF K^+ AND Cl^- IONS IN COMPRESSED WATER

M. NAKAHARA, *Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, JAPAN*

The limiting molar conductances λ_o of K^+ and Cl^- ions have been determined in D_2O and H_2O at 25 ^oC, as a function of pressure up to 2 kbar, from the measured conductances and transference numbers of KCl. [1] From λ_o the friction coefficients ζ are calculated. The hydrodynamic frictions ζ_s due to Stokes' laws for perfect slip are subtracted to obtain the residual friction coefficients $\Delta\zeta$. The results obtained are used to test the Hubbard-Onsager (HO) dielectric friction theory.[2]

At atmospheric and high pressures $\Delta\zeta$ of the K^+ ion in D_2O, denoted by $\Delta\zeta(K^+/D_2O)$, is larger than $\Delta\zeta(K^+/H_2O)$ just as predicted by the HO theory. This demonstrates that the solvent isotope effect is brought about through the bulk viscosity of the solvent because the Hubbard-Onsager radius is the same for both isotopes.

On the other hand $\Delta\zeta(Cl^-/D_2O)$ is lower than $\Delta\zeta(Cl^-/H_2O)$, contrary to the theoretical prediction because the sphere-in-continuum model takes no account of the different signs of the ion charge. The reverse solvent isotope effect has been explained by considering a microscopic viscosity, in the vicinity of the relatively large ion, which is considerably smaller than the bulk viscosity. The smaller microscopic viscosity arises from the structure of the hydration shell around the Cl^- ion which is markedly different from the structure of the first coordination shell in pure water. [3]

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4-6 (O) CONDUCTANCE BEHAVIOUR OF SOME SILVER(I) SALTS IN WATER-ACETONITRILE AND METHANOL-ACETONITRILE MIXTURES

C. KALIDAS and S. SUBRAMANIAN
Department of Chemistry, Indian Institute of Technology,
Madras-600 036, INDIA

Conductance measurements on electrolytes provide valuable information on the selective solvation of the ions in mixed solvents. [1,2] In the present work, the conductance behaviour of silver(I) bromate and silver(I) perchlorate in water-acetonitrile(AN) mixtures and that of silver(I) bromate, acetate and perchlorate in methanol-AN mixtures has been investigated over the entire range of solvent compositions. The data were analysed by the 1980 Fuoss equation [3] and the limiting molar conductivities (Λ_o) and ion-association constants (K_A) were evaluated in all the solvent mixtures. Using transference number data derived from a concentration cell with transference, the Λ_o values of all the salts were split into their ionic contributions and the corresponding Walden products evaluated. That of silver ion was found to decrease sharply with the addition of AN in both the mixed solvent systems and has been interpreted in terms of the selective solvation of silver ion by AN in these mixtures. The anionic Walden products, however, vary in a more complex manner and it appears that structure-breaking and structure-making effects of the ions play a major role in their variation with solvent composition. The K_A values were generally found to decrease with the addition of AN, pass through a minimum and then increase, which is indicative of hetero-selective solvation of the electrolytes in these mixed solvents.

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4-7 (O) TRANSFERENCE NUMBERS IN CONCENTRATED ALKALI CHLORIDE SOLUTIONS

M. SPIRO, D. PANOPOULOS, and H. KANEKO

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

Concentrated electrolyte solutions are important in nature and in many industrial processes as well as being of considerable interest in their own right. An international effort is currently under way to measure their transport properties and to derive from them the corresponding phenomenological transport coefficients. For this purpose conductances, diffusion coefficients, and transference numbers are all required, but transference numbers are the quantities in shortest supply.

We have recently modified the moving boundary method to make it more applicable to concentrated solutions [1] but now prefer the e.m.f. method using cells with transference. Because of doubts expressed about the suitability of AgCl/Ag electrodes in concentrated chloride solutions we have instead employed chlorine electrodes in cells of the type

$$\mathrm{Pt/Ir} \,|\, \mathrm{Cl_2} \,|\, \mathrm{MCL}\ (m) \,|\, \mathrm{MCl}\ (m_{ref}) \,|\, \mathrm{Cl_2} \,|\, \mathrm{Pt/Ir}.$$

The solubility of chlorine is lowered by using $Cl_2 + N_2$ mixtures. Even so, hydrolysis of chlorine is sufficiently repressed only above ca. 2 m chloride. Experiments with aqueous HCl from 2 to 8 m at 25 °C have yielded transference numbers in good agreement with values obtained by the use of H_2 electrodes [2,3] while they differ somewhat from published values determined with AgCl/Ag electrodes. We now present transference numbers for aqueous KCl solutions up to 4.5 m at 25 °C for which almost no previous data exist, and also for aqueous NaCl solutions up to 6.0 m at 25 °C. Several discordant sets of transference numbers have been published for concentrated NaCl solutions: our results agree with three of these but differ from two other sets. These discrepancies the results themselves will be discussed.

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4-8 (O) AQUEOUS SOLUTIONS OF ZINC HALIDES: AN EXCEPTIONAL CLASS OF ELECTROLYTES

H. WEINGÄRTNER and K.J. MÜLLER
Institut für Physikalische Chemie und Elektrochemie der
Universität, Kaiserstr. 12, D-7500 Karlsruhe, F.R.G.

Transport coefficients (conductance, viscosity and tracer diffusion) in aqueous solutions of $ZnCl_2$, $ZnBr_2$ and ZnI_2 exhibit some exceptional features, which can be contrasted with the behaviour of aqueous $MgCl_2$ and $CdCl_2$. In dilute solutions the zinc salts behave as normal 2:1-electrolytes with complete dissociation into ions. At higher concentrations they behave more like 1:1-electrolytes. The onset of complex formation (above 0.1 mol dm^{-3}) occurs rather suddenly and causes inflections in the concentration dependence of the transport coefficients, which have not yet been observed for other systems. This abnormal behaviour is also observed in the osmotic coefficients and in the chemical shift of water protons in these solutions. However, the onset of complex formation affects the various coefficients differently, i.e. they exhibit different sensitivities to the formation of ion association. It is therefore doubtful whether sets of stability constants can be found which represent all properties unambiguously.

4-9 (O) IONIC SELF-DIFFUSION IN THE METHANOL-WATER-NaCl SYSTEM

E. HAWLICKA* and W. REIMSCHÜSSEL
Institute of Applied Radiation Chemistry, Technical University
Lodz, POLAND

The open capillary method was used to investigate ionic self-diffusion processes in the methanol-water-NaCl system at 298 K. The self-diffusion coefficients of sodium and chloride ions have been determined as a function of salt concentration (5.10^{-5} - 10^{-1} mol dm^{-3}), over the whole range of solvent composition. The limiting self-diffusion coefficients of the ions D_i^{∞} were calculated by means of the Robinson and Stokes approximation.

The D_i^{∞} values for sodium and chloride ions vary with the mole fraction of methanol, x_M, and through minima at x_M about 0.5 and 0.4, respectively.

The previously-reported data of the sodium and iodide self-diffusion coefficients in the methanol-water-NaI system have been recalculated. The same values of D_{Na+}^{∞} were found in both the systems studied. The products of the D_i^{∞} values and the solvent viscosity η_o have been calculated. The relation between the $D_i^{\infty}\eta_o$ product and the hydrodynamic radius of an ion has been discussed. A significant influence of solvent composition on the ionic radius was observed. An excellent correlation was found between the hydrodynamic radii of ions and $\Delta H^{\ominus}_{trans}$ and $\Delta S^{\ominus}_{trans}$ from water into methanol-water mixtures.

*Present address: Max-Planck-Institut für Chemie, Saarstrasse 23, 6500 Mainz, F.D.R.

4-10(O) POLYAROMATIC COMPOUNDS AS HIGH TEMPERATURE SOLVENTS FOR IONIC SALTS

G. GEBLEWICZ, R. POTTER, D. SCHIFFRIN
The Chemistry Department, University of Southampton, SO9 5NH, Hants, ENGLAND

Heath et al. [1] showed originally that molten naphthalene and the 1-chloro and 1-methyl derivatives were surprisingly good solvents for tetraalkylammonium salts, which gave solutions of good conductivity.

In the present work, the solvent properties of 12 high boiling point polycyclic aromatic compounds were studied at a temperature of 150 °C. It has been found that some simple inorganic salts e.g. LiCl, KCl, KBF_4, $NaBF_4$ and KF display a significant solubility in these non-polar solvents such as m-terphenyl, acenaphthene, biphenyl, fluoranthene, fluorene.

The conductivities however, are very low, indicating that extensive ion pairing in solution occurs. The solubility data has been analysed using the solvation model of Abraham. Solubility is dependent on the lattice energy, ionic size and solvent dielectric properties. Tetraalkylammonium salts give conducting solutions in these solvents. The ion-ion interactions for these systems will be discussed.

The possibility of using these new solvents as media for electrochemical studies will be outlined.

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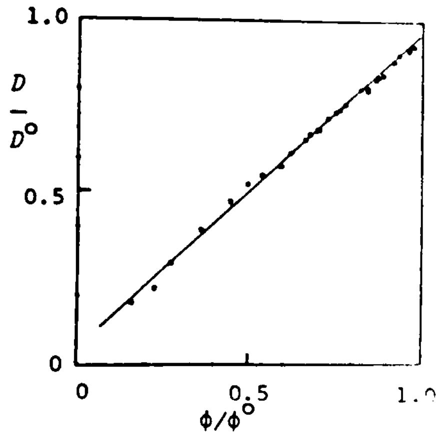
4-11(O) PHENOMENOLOGICAL RELATIONSHIP BETWEEN THE FLUIDITY AND MOBILITY IN CONCENTRATED ELECTROLYTE SOLUTIONS

KAZUKO TANAKA and REITA TAMAMUSHI
The Institute of Physical and Chemical Research, 2-1 Hirosawa,
Wako, Saitama 351-01, JAPAN

The effect of fluidity on the mobilities of component species in solution is an important problem in theories of electrolytic conductance and diffusion. The best known and classical relationship between the fluidity and mobility is given by the Stokes-Einstein equation, $D = kT\phi/a\pi r$, where D is the diffusion coefficient, ϕ is the fluidity, r is the radius of the diffusing species, a is a constant, and the other symbols have their usual meanings. A similar equation is known for the ionic mobility. In this study we have examined some empirical correlations between the fluidity and diffusion coefficients or ionic mobilities in concentrated solutions.

A very good linear correlation, as shown in the figure, was observed between the relative fluidity and the relative self-diffusion coefficient of Cl^- in aqueous solutions of various concentrations of LiCl, NaCl, $MgCl_2$, $CaCl_2$ and $BaCl_2$. Here D^o is the self-diffusion coefficient of Cl^- at infinite dilution and ϕ^o is the fluidity of water. The Stokes-Einstein equation with a=4 gave a reasonable radius of 1.6 Å for Cl^- in solution.

Self-diffusion coefficients and molar conductances of so-called structure-making species were found to satisfy similar linear relationships to that shown in the figure. On the other hand, transport properties of ions such as K^+, Rb^+, Cs^+ and their salts exhibited significant deviations from the linear relationship between fluidity and mobility.



Theoretically no direct relationship may be expected in concentrated solutions. Nevertheless, such empirical relationships obviously do exist and will provide useful information for the study of concentrated solutions.

4-12(O) A NEW THEORY OF THE VISCOSITIES OF ELECTROLYTE SOLUTIONS

D. FEAKINS[+], W.E. WAGHORNE[+] and K.G. LAWRENCE[*]
[+] *Department of Chemistry, University College, DUBLIN 4.*
[*] *Department of Chemistry, Birkbeck College, London WC1E 7HX, U.K.*

For many years the lowering the viscosities of water and mixed aqueous solvents by certain electrolytes has been attributed to the breaking down of the three dimensional structure of the stationary or ground state solvent.

Recent work has cast considerable doubt on this explanation. For example, the fact that the ionic molar contribution to the free energy of activation for viscous flow is negative for CsCl in some water + t-butanol [1] mixtures cannot be explained in this way. Moreover the theoretical work of Ben-Naim [2] has shown that the free energy of solution, and by implication the free energy of activation for viscous flow, is independent of solute-induced structural changes in the solvent, such as those proposed, say, by Frank and Wen. [3]

In this paper the problem is re-examined, with particular attention to the nature of the transition state for viscous flow. It is proposed that ions increase the fluidity of the solvent by increasing their coordination in the transition state rather than by disrupting the structure of the ground state solvent.

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4-13(O) CONTRIBUTIONS OF LONG-RANGE SOLVENT PERTURBATIONS TO VISCOSITIES AND VOLUMES OF ELECTROLYTE SOLUTIONS

Wolfhart SEIDEL
Physikalisch-Chemisches Institut Universität Giessen,
Heinrich-Buff-Ring 58, D - 6300 Giessen, F.D.R.

Even at very low concentrations, viscosities and apparent molar volumes are sometimes found to deviate appreciably from theoretical expectations. The viscosity B coefficients of several ions are actually negative, so that the physical meaning of the original Einstein model is lost. It is well-known that such deviations are usually explained as being due to ion-solvent interactions. On the other hand, the deviations are sometimes attributed in a more or less arbitrary manner to the ions alone, at most including a solvation sphere. The outer solvent is supposed to be a merely static and continuous system. This view is supported by the common short-range and long-range classification of molecular and ionic interaction forces.

Although these classifications may be good concepts at the level of single particles or isolated pairs, they seem doubtful for closely coupled multi-molecular entities like solutions of associating liquids. At least on a short time scale (fast dynamics), intermolecular coupling should result in a space-filling network of several subsystems or domains. But even during short times, long-range perturbations spread from ions or other sources of strong perturbation potential and result in distributional shifts. These shifts will give rise to additional changes in the physical properties of the whole system which cannot be well explained in the framework of electrolyte theory.

Some recent experimental results are discussed on the basis of a long-range solvent perturbation model.

4-14(O) COMPARISON OF VISCOSITY AND ENTHALPY OF DISSOLUTION OF 1:1 AND 2:1 ELECTROLYTES IN WATER-ORGANIC SOLVENT MIXTURES

S. TANIEWSKA-OSINSKA, A.KACPERSKA, J. BARCZYNSKA, M JÓŹWIAK,
B. NOWICKA

Department of Physical Chemistry, University of Lodz,
91-416 Lódź, POLAND

Viscosities of water + ethanol, water + tetrahydrofuran and water + hexamethylphosphortriamide systems were measured. Viscosities of dilute NaI solutions in the same solvent mixtures and of $CaCl_2$ in water-ethanol mixtures were measured at 20, 25 and 30 °C using an Ubbelohde viscometer.

Plots of relative viscosity, η_r, against mole % of organic component in the mixtures are presented. The results are interpreted in terms of the effect of 1:1 and 2:1 electrolytes on the properties of water-organic systems. A comparative analysis is carried out of viscosity coefficients and standard solution enthalpies for the electrolytes studied in these water-organic solvent mixtures. [1-4] Some suggestions are made about the effect of organic solvents on the structure of water.

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4-15(O) STUDIES ON SOLUTE-SOLVENT INTERACTIONS FROM VISCOSITY MEASUREMENTS WITH PARTICULAR REFERENCE TO HIGH CONCENTRATION RANGE OF ALKALI HALIDES IN AQUEOUS LACTOSE SOLUTION

Awadhesh K. SINGH, Prem N. TRIPATHI and Vinod K. SINGH
Department of Chemistry, Harish Chandra Postgraduate College,
Varanasi-221 001, INDIA

Numerous studies have shown that viscosity measurements are useful in providing information regarding solute-solvent interactions, and particularly as regards the modifications induced by ions on the structure of solutions. The viscometric technique has generally been used in studying the behaviour of electrolytes in pure solvents, but investigations of multi-component solutions are rather scanty. Although there are very few data available on the thermodynamic and transport properties of aqueous solutions of mixtures of electrolytes and nonelectrolytes, these mixtures provide a wealth of information about the interaction of various functional groups with ions.

In the present work, relative viscosities (η_r) of concentrated solutions of sodium and potassium halides (concentration range 0.125 to 3.0 M) in aqueous lactose solution at 25, 30, 35 and 40 °C are reported. Viscosity data have been analysed using Vand's, Thomas's, Bresslau and Miller's, Moulik's and a generalised treatment, at higher electrolyte concentrations. The molar volumes($\bar{V}$), ionic coefficients ($B_{\pm}$) and hydration numbers (n_B) of ions were computed, and structural aspects of alkali metal halides in aqueous lactose solution have been interpreted by taking into account the magnitude of the various parameters obtained. The temperature dependence and structural aspects of ionic B-coefficients ($B_{\pm}$) have also been discussed. On the basis of the data, it has been found that in 0.5 M lactose solution, different ions show a structure-breaking tendency in the order: $I^- > Br^- > Cl^- > K^+ > Na^+$.

THEME 5

Thermodynamic properties

ORAL CONTRIBUTIONS

5-1 (O) THE DEBYE-HUCKEL PARAMETERS FOR ELECTROLYTE SOLUTIONS

Robert L. KAY
Carnegie-Mellon University, Department of Chemistry,
4400 Fifth Avenue, Pittsburgh, Pa. 15213 U.S.A.

The Debye-Hückel parameters can be used to extrapolate thermodynamic data for dilute solutions of electrolytes provided that the first and second derivatives of the dielectric constant with respect to temperature and pressure are known for the particular temperature and pressure involved. However, such data are difficult to come by and often require the joining of data from various workers for different ranges of temperature and pressure.

Recently Bradley and Pitzer have collected the best data for water at temperatures up to 350 °C and 1 kbar and have recalculated the Debye-Hückel parameters. They used a Tait equation for the pressure dependence and an exponential equation for the temperature dependence of the absolute dielectric constants. It will be shown that the use of absolute values of the dielectric constants introduces unnecessary error in the derivatives. These errors can be avoided by using dielectric increments rather than the absolute values. Similar evaluations for non-aqueous solvents will be presented.

5-2 (O) HYDRATION OF CATIONS AND ITS ROLE IN THEIR ADSORPTION ON OXIDES

M. A. MALATI
Mid-Kent College of Higher and Further Education, Chatham,
ME5 9UQ, U.K.

A calculation of hydrated radii of alkaline-earth ions [1] was extended to some divalent ions [2]. The values will be compared to some published data. Based on our values, the adsorption of cations by quartz, silica or manganese dioxide was ascribed to an ion-exchange between hydrated ions in the outer Helmholtz layer and in the bulk solution [3-5]. Similar arguments explained the heats of adsorption on these oxides [5-7] and the activation of the oleate flotation of pyrolusite and of quartz [7,8]. Solute-solute interactions were suggested for the latter systems. The limitations of the mechanism in the case of some divalent ions adsorbed on silica are discussed [9]. The opposite trends for the adsorption of cations on rutile or anatase is tentatively explained [10,11].

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5-3 (O) THERMODYNAMIC MOLAR PROPERTIES OF AQUEOUS NONELECTROLYTE SOLUTIONS USING SOUND VELOCITY MEASUREMENTS

Mostafa M. EMARA and Nazik A. FARID
Department of Chemistry, Faculty of Science, AlAzhar University
Nasr City, Cairo, EGYPT; and Egyptian Petroleum Research
Institute, Nasr City, Cairo, EGYPT

Partial molar volumes and adiabatic compressibilities were calculated from measurements of the densities and ultrasonic velocities at various concentrations of aqueous solutions of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, triethanol amine, ethylene diamine tetra-2-ethanol and ethylene diamine tetra 2-propanol.

The values of the partial molar volumes at infinite dilution and the apparent molar compressibility at infinite dilution were obtained from ϕ_V against c plots.

The results are explained in the light of solute-solute, and solute-solvent interactions.

5-4 (O) TEMPERATURE DEPENDENCE OF DENSITY, PARTIAL VOLUME, AND EXPANSIVITY OF LIQUIDS, LIQUID MIXTURES, AND SOLUTIONS

H. CRAUBNER
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, F.D.R.

The systematic investigation of fluids and their interactions by statistical thermodynamics requires knowledge of the volumetric properties as a function of temperature. Information on the coupling between the mechanical and the thermal properties can be obtained ***via*** the thermal expansivity. A densitometer device is described for the determination of the temperature dependence of density, partial specific volume, and isobaric expansivity of solids, liquids, liquid mixtures and solutions. The densitometer is based on the hydrostatic method and employs a two-chamber measuring system and an electronic balance. It can be used at both low (down to -100 °C) and high (up to 250 °C) temperatures. A small, optically-polished buoyancy body of fused silica serves as a calibration standard.

The temperature dependence of density, partial specific volume and expansivity of liquids, liquid mixtures and solutes can be calculated, from the appropriate theoretical relationships, from densitometric scanning experiments.

Information will be presented on several systems including the following:

a) n-hexane; toluene; methanol (and mixtures of these)

b) methanol-water mixtures and

c) solutions of poly(methylmethacrylate) in toluene at low temperatures.

The results demonstrate that the densitometer is of high precision and very suitable for the absolute determination of both the density and the thermal expansion of small fluid samples (ca. 6 up to 100 cm^3) as a function of temperature. Self-consistent density determinations relative to the calibration standard can be carried out with a precision of (<±0.01 %). Absolute densities have an accuracy of <±0.1 %.

5-5 (O) THERMODYNAMICS OF SOLUTIONS FROM THE GRAND PARTITION FUNCTION AT THE McMILLAN-MAYER (MM) LEVEL: RELATIONSHIP WITH THE FRIEDMAN EXCESS FUNCTIONS

J.L. GÓMEZ-ESTÉVEZ
Departamento de Termología, Facultad de Física, Universidad de Barcelona, Diagonal-645.08028 Barcelona, SPAIN

The McMillan-Mayer theory shows that the grand partition function at the MM level (Ξ_{MM}) for a system with component σ as a solute in the solvent w is [1,2]:

$$\Xi_{MM} = \sum_{N_\sigma \geq 0} \frac{(z_\sigma/\gamma_\sigma^o)^{N_\sigma}}{N_\sigma!} \int \exp[-\beta W_{N_\sigma}^{\infty}]\, d\{N_\sigma\} \qquad (1)$$

where z_σ is the activity of the solute, γ_σ^o the activity coefficient of the solute at infinite dilution (referred to an ideal gas scale) and $W_{N_\sigma}^{\infty}$ is the potential of mean force among N_σ solute molecules at infinite dilution ($z_\sigma \to 0$).

By formulating the thermodynamics of a solution in osmotic equilibrium with a pure solvent phase, a recipe is given for obtaining certain "excess" functions from Ξ_{MM} (eq.1):

$$kT\left(\frac{\partial \ln \Xi_{MM}}{\partial \mu_w}\right)_{T,V,\mu_\sigma} = N_w - N_w^* \qquad (2) \qquad\qquad kT\left(\frac{\partial \ln \Xi_{MM}}{\partial \mu_\sigma}\right)_{T,V,\mu_w} = N_\sigma \qquad (3)$$

$$kT\left(\frac{\partial \ln \Xi_{MM}}{\partial V}\right)_{T,\mu_w,\mu_\sigma} = \pi \qquad (4) \qquad\qquad \left(\frac{\partial kT \ln \Xi_{MM}}{\partial T}\right)_{V,\mu_w,\mu_\sigma} = S - S^* \qquad (5)$$

where N_w, N_w^*, are the number of solvent molecules in the solution and in the pure solvent phase respectively; N_σ is the number of solute molecules, π the osmotic pressure and $S-S^*$ the difference between the entropies of the solution and the pure solvent.

Finally, the links between (1) and the excess functions, as used by Friedman [2,3] are presented and discussed.

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5-6 (O) SOLVENT EFFECTS ON THERMODYNAMICS OF SINGLE IONS

Mahmoud M. ELSEMONGY[a], Mohamed A. HUSSEIN[b] and Fikry M. REICHA[c]

[a]*Chemistry Department, College of Science, King Saud University,*
P.O. Box 2455, Riyadh-11451, KINGDOM OF SAUDI ARABIA

[b]*Chemistry Department, Faculty of Science, Kuwait University,*
P.O. Box 5969, KUWAIT

[c]*Physics Department, Faculty of Science, Mansoura University, Mansoura,*
EGYPT

Recently, a new method has been developed [1] for the determination of absolute electrode potentials and the thermodynamics of single ions in solution. It has been successfully applied to the cells:

Pt | H_2(g, 1 atm) | HX, solvent | AgX | Ag and

M | MX, solvent | AgX | Ag, in aqueous and methanol + water systems. The studies have been extended to other solvent systems, including both protic and aprotic, partially aqueous and non-aqueous solvents. The results show the same general trends and reflect the same interesting features obtained earlier. [1] All gave evidence that the plots of standard transfer free energy or entropy against the reciprocal of the anionic or cationic radius, which were used earlier [2] to obtain the thermodynamic properties of single ions, cannot be accepted.

The standard Gibbs energy of transfer (and similarly the entropy and enthalpy of transfer) can be split [3] into two parts, a chemical part and an electrostatic (ΔG^{o}_{el}) which is calculated from the (inadequate) Born equation.

However, a new equation, correlating the cell (or electrode) potential with dielectric constant of the solvent, has been developed and used to calculate the chemical contribution to the transfer thermodynamic quantities of single ions in various solvents. The results show that the ΔG^{o}_{el} values should in fact account for all the interactions between the charge on the ion and the totality of charges on the solvent molecules, of which the Born contribution plays but a minor role.

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5-7 (O) SOLVENT EFFECTS OF THE ELECTROCHEMICAL OXIDATION OF CHROMIUM PENTACARBONYL COMPLEXES $Cr(CO)_5L$

M.A. SANTA ANA, I. CHADWICK, C. DIAZ, N. YUTRONIC and G. GONZÁLEZ
Department of Chemistry, Faculty of Science, University of Chile,
Casilla 653, Santiago, CHILE

The stability and the reactivity of metal-organic complexes depend on the charge distribution in the molecule which in turn can be affected by the medium. Attempting to study the effect of the medium on the properties of carbonyl compounds, we have investigated the influence of various aprotic solvents on the electrochemical oxidation of the monosubstituted chromium complexes $Cr(CO)_5L$ [L = CO, PPh_3, PEt_3, $S(NC_4H_8O)_2$, $S(N(CH_2Ph)_2)_2$, $SC(NMe_2)_2$, $SC(NEt_2)_2$, and $SC(NH_2)_2$].

The oxidation potentials of the complexes - obtained from reversible waves in cyclic voltammograms and measured against bis-biphenylchromium(I) as internal reference - depend on the nature of the ligand L as well as on the properties of the solvent. Thus, for every compound a different but always nearly linear relationship of the oxidation potential with the solvent basic strength (expressed as the Gutmann's donor number DN) was observed:

$$E_p^{ox} = a_0 + a_1 DN$$

From these relationships it is possible to estimate the oxidation potentials of the complexes in a hypothetical inert medium (DN=0), a_0, as well as their sensitivity to the solvent, a_1.

The comparison of the potentials at DN=0 with the acceptor capability of the ligands - obtained independently as the Graham's parameter π from the I.R. spectra of the ligands in the same complexes in n-hexane - indicates that both values are directly related. As expected from the description of the bonding in metal carbonyl compounds by the limiting structures.

$$\overset{\delta^+}{O\equiv C}-\overset{\delta^-}{M}=L \qquad \text{and} \qquad O=C=M=L$$

the ease of oxidation of the complexes decreases with increasing π-acceptor capability of the ligand L. On the other hand, the sensitivity of the complexes with sulphur ligands to the solvent is also a smooth function of the effectiveness of the ligand as a π-acceptor.

Our results, as well as other medium effects reported in the literature, can be rationalized by considering an outer-sphere interaction mechanism

$$D\rightarrow O-C-M-L$$

where the actual charge distribution would result from an equilibrium between σ and π effects modulated by the nature of the ligand L.

5-8 (O) SOLVENT-SOLVENT AND SOLVENT-SOLUTE INTERACTIONS IN PROTIC AND APROTIC SYSTEMS

S. WASIF[1], S.B. SALAMA[1], S. ELKADRY[2] and O. DABBIT[2]

[1]*Zagazig University, Zagazig, EGYPT*

[2]*Aleppo University, Aleppo, SYRIA*

Thermodynamic studies on weak complexes of the types: $SO_2.X^-$, $SOCl_2.X^-$, $SOBr_2.X^-$ and $SO_2Cl_2.X^-$(X=Cl,Br & I) in the mixed solvent MeCN-DMSO show the influence of solvent-solvent interactions on the stabilities of these species in the solvent mixtures.

Interactions between the aprotic solvents MeCN and DMSO were shown to exist by several techniques; viz., dielectric constants, refractive indices, density, viscosity, vapour pressure and spectroscopy.

Solute-solvent interactions were inferred from halide ligand replacement in the above complexes when mixed solvents are used. They could be deduced from spectroscopic observations on SO_2 solutions in MeCN, DMSO and their mixtures. Similar behaviour is observed for other sulphur compounds in the same solvents.

Further studies on the ionization of the weak acids: phenols and benzocyclobutenones, in water-organic solvents mixtures confirm the presence of interactions between water and organic solvents such as MeOH, EtOH, PrOH, acetone, DMF and DMA.

Interactions between water and different organic solvents were confirmed from viscosity, thermal, conductance and other measurements.

Whether mixtures were protic or aprotic, enthalpy and free energy changes could help in describing such interactions. Entropy changes do not offer a simple explanation of such system.

5-9 (O) TEMPERATURE DEPENDENCE OF SOLUTE-SOLUTE AND SOLUTE-SOLVENT INTERACTIONS IN AQUEOUS SOLUTIONS OF THE HOMOLOGOUS SERIES OF n-DODECYLPOLYETHYLENEGLYCOL SURFACTANTS, $C_{12}EO_m$(m=4,5,6 and 8)

T.M. HERRINGTON and <u>S.S. SAHI</u>
Department of Chemistry, University of Reading, Reading RG6 2AD, ENGLAND

Nonionic surfactants, like ionic surfactants, form micelles above a critical concentration in water with liquid crystals frequently occurring at higher concentrations. However. many are unusual in having a lower consolute temperature; when the temperature is increased, the solution becomes turbid in a narrow temperature range, called the cloud point. Above the cloud point the system separates into two isotropic solutions. This behaviour is shown by the $C_{12}EO_m$ series. The micellar properties have been much studied in the vicinity of the cloud curve. Light scattering and sedimentation methods were used in the 60's and more recently there has been a very active literature including neutron scattering, nmr and dynamic light scattering methods. The results of these studies have not resolved the fundamental issue of the effect of temperature in causing predominantly micellar growth *or* increasing the strength of the interactions between small micelles.

The number average micellar molar masses of the $C_{12}EO_m$ (m = 4,5,6 and 8) series were determined over the temperature range 0 to 70 °C. The micellar aggregation numbers did not increase significantly with temperature. The aggregation numbers decrease as m increases in accordance with theories of micelle formation. Thermodynamic data on the systems were analysed using accepted theories of dilute solutions. The overall picture presented is that, with increasing temperature, dehydration of the polyoxyethyleneglycol molecule occurs together with increasing intermicellar attraction.

5-10(O) SOLUTE-SOLUTE INTERACTIONS OF ORGANIC MODEL COMPOUNDS IN NONAQUEOUS SOLVENTS: RELEVANCE FOR THE NATIVE CONFORMATION OF PROTEINS

M. BLOEMENDAL and G. SOMSEN
Department of Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam, THE NETHERLANDS

By means of microcalorimetric procedures, enthalpies of dilution have been measured for a number of organic solutes in the aprotic solvent N,N-dimethylformamide (DMF) and the protic solvent N-methylformamide (NMF). The solvents were chosen to represent an amidic environment for the solute molecules which bears some resemblance to the interior of globular proteins. From the experimental results, enthalpic interaction coefficients have been calculated on the basis of the McMillan-Mayer theory of dilute solutions.

The discussion will mainly be focussed on the enthalpic pair interaction coefficients, B_2^h. Generally, values of B_2^h in the solvent DMF are negative, indicating that the corresponding solute-solute interactions are energetically favourable. In the solvent NMF both negative and positive values of B_2^h are found. In both solvents B_2^h becomes more negative when the size of the solute molecules increases. The trends in both solvents are comparable. In DMF the value of B_2^h for urea deviates considerably. For this small molecule an extraordinary large negative value has been found. To a lesser extent deviations also seem to occur for larger molecules and an example will be mentioned which may be relevant for the native conformation of proteins.

The combined results show that the enthalpies of interaction are determined by different effects e.g. solvophobic interaction, and solvation, as well as preferential orientation of the solute molecules, may play a role.

5-11(O) PREFERENTIAL SOLVATION AND HYDROPHOBIC HYDRATION OF SACCHARIDES IN MIXTURES OF N,N-DIMETHYLFORMAMIDE AND WATER

R.W. BALK and G. SOMSEN

Department of Chemistry, Free University, De Boelelaan 1083,
1081 HV Amsterdam, THE NETHERLANDS

The course of the enthalpy of solution (or transfer from pure water to the mixture: W → M) of some simple saccharides versus the mole fraction of water, x_W, in mixtures (M) of N,N-dimethylformamide (DMF) and water (W) is characterized by an exothermic curvature at low water content and (larger) exothermic shifts in the water-rich region. In this respect, these curves are quite similar to those of polyols, alcohols, ureas and amides. [1,2,3] The exothermic curvature is considered to result from preferential hydrogen bonding of the hydroxy groups and the exothermic shifts from hydrophobic hydration of the apolar groups on the solute molecules. The two effects are correspondingly described by a thermodynamic theory of preferential solvation, as derived by Covington and coworkers and a simple hydrophobic hydration model, as derived by our group. The resulting model appears to give a good description of the experimental curves.

Both the experimental results and those derived from the analysis of the enthalpy curves with this model, permit several conclusions.

(i) The solvation behaviour of saccharides (and polyols) in the studied solvent mixtures is quite similar to that of other nonelectrolytes: it is characterized by preferential solvation of functional groups and hydrophobic hydration of apoloar sites.

(ii) The extent and balance of these two effects appear to be unique for each solute and depend also on stereochemical detail. For the saccharides this dependence is larger than for the polyols.

(iii) In the DMF/W mixtures, the hydroxy groups of the saccharides are preferentially hydrated. This effect seems to be larger for the axial than for the equatorial hydroxy groups, because it increases in the order β-D-glucose < α-D-glucose < (α-)D-galactose.

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5-12(O) SOLUTE-SOLUTE, AND SOLUTE-SOLVENT INTERACTIONS IN AQUEOUS SOLUTIONS OF AMINO ACIDS AND PEPTIDES

R. SYKES and I.D. WATSON
Department of Chemistry, Massey University, Palmerston North, NEW ZEALAND

We wish to report on some of our recent measurements of vapour pressures and densities of amino acid and dipeptide solutions over a temperature range. We shall use the data to find the osmotic coefficients and partial molar volume of the solute at infinite dilution, and shall use these values to obtain a measure of the solute-solute, and solute-solvent interactions in such systems. The results will be interpreted in terms of perturbated hard sphere approach, and dipole-dipole interactions.

POSTER CONTRIBUTIONS

2-1 (P) METROPOLIS-MONTE CARLO LIQUID WATER SIMULATION WITH FOUR-BODY INTERACTIONS INCLUDED

J. DETRICH, G. CORONGIU, and E. CLEMENTI

IBM Corporation, DSD, Department 48B/MS 428, Neighborhood Road, Kingston, NY 12401, U.S.A.

A four-body interaction potential for water molecules is derived. The new terms are combined with previously-developed two- and three-body potential terms and applied in a Metropolis-Monte Carlo simulation at 298 K for an (N,V,T) ensemble with 512 water molecules. Improvements, relative to the results using only two-body, or two- and three-body interactions, are reported for the correlation function g(0-0), for the X-ray and neutron beam scattering intensities, and for the enthalpy.

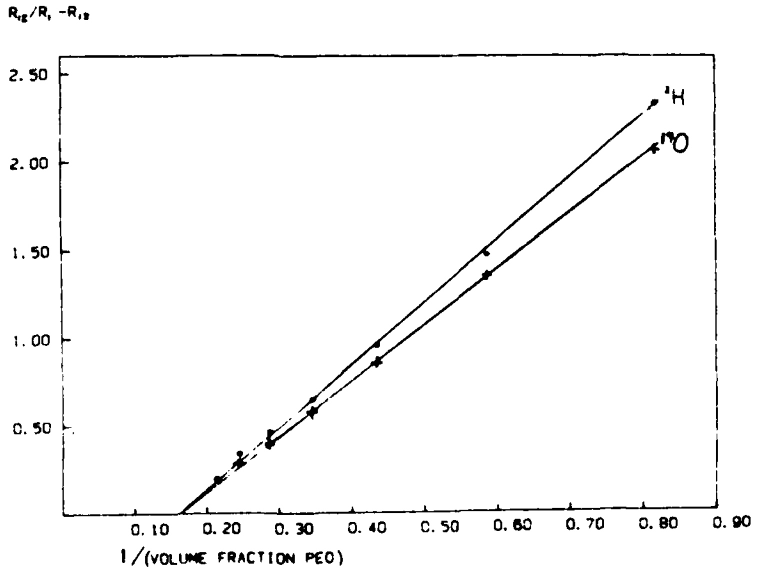
2-3 (P) POLYETHYLENEOXIDE (PEO)-WATER INTERACTIONS STUDIED BY NUCLEAR MAGNETIC RELAXATION

J. BREEN, L. HUIS, D. van DUIJN and J.C. LEYTE
Gorlaeus Laboratories, Department of Physical and Macromolecular Chemistry, P.O. Box 9502, 2300 RA Leiden, THE NETHERLANDS

The dynamic behaviour of water molecules may be studied by both ^{2}H- and ^{17}O relaxation rate measurements. [1] The relaxation rate depends strongly on the presence of PEO. Strong PEO-water interactions are responsible for this phenomenon. [2] The nuclear relaxation rates provide information about the water-polymer interaction volume, the polymer volume and the water relaxation rates in the neighbourhood of the polymer. The interpretation is complicated by excluded volume effects.

Some characteristic data are presented in the figure. The solvent is described using a two-phase model (free water and water interacting with PEO). The experimental relaxation rate is separated into a "free" water part and a "bound" water part. The fraction of the "bound" phase is taken to be the quotient of the total volume minus the polymer volume (free-volume) and the polymer-water ("bound") volume. Information is obtained about polymer dimensions, the range of polymer-water interactions and the retardation of the water dynamics near the polymer.

1. C.W.R. Mulder, J. Schriever and J.C. Leyte, *J. Phys. Chem.*, 87, 2336 (1983).
2. G.N. Malcolm and J.S. Rowlinson, *Trans Faraday Soc.*, 53, 921 (1957).



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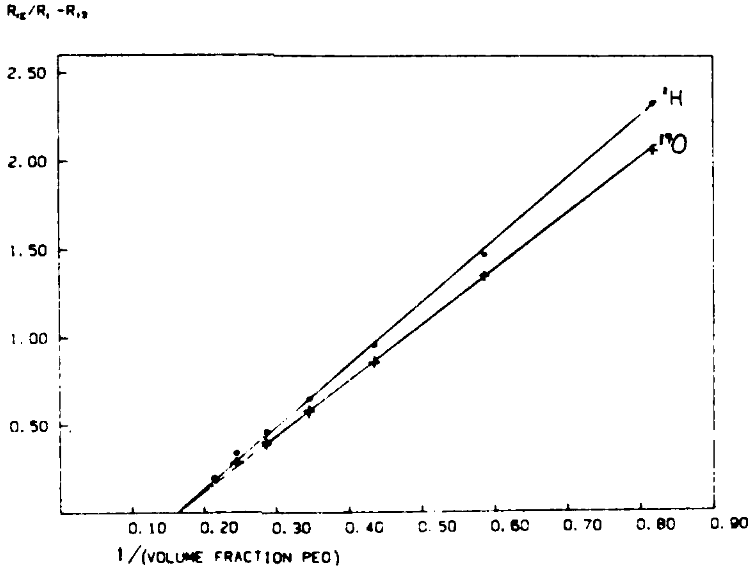

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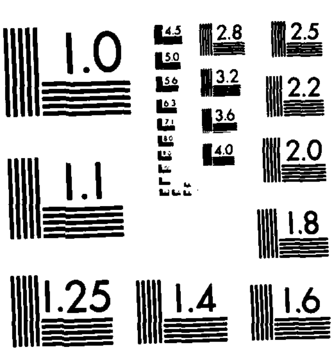

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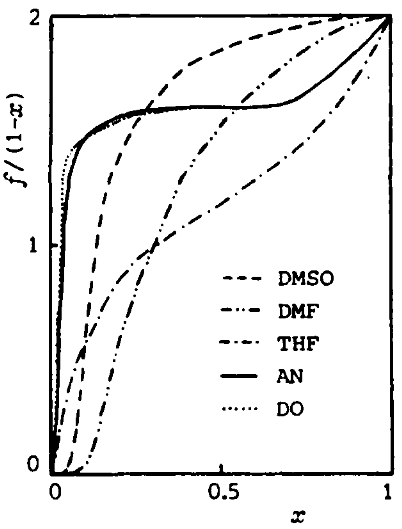
2-4 (P) STRUCTURAL FEATURES OF BINARY AND TERNARY MIXTURES OF WATER WITH NON-ELECTROLYTES

Piero MIRTI and Vincenzo ZELANO
Dipartimento di Chimica Analitica, Università di Torino, via Giuria 5, 10125 Torino, ITALY

The average number, f, of water-to-water hydrogen bonds broken by one molecule of non-electrolyte has been calculated for a series of binary mixtures containing water together with dimethylsulfoxide, dimethylformamide, tetrahydrofuran, 1,4-dioxan or acetonitrile [1] and for the ternary system water-DMSO-dioxan. [2] The values of f have been obtained from nmr data of the chemical shift of the hydroxyl protons and changes of this with the mole fraction, x, of the non-electrolyte, reaching a maximum at intermediate compositions. Dioxan and acetonitrile show maximum capability in relatively dilute solutions ($x < 0.2$), whereas for the other non-electrolytes maximum f is lower and shifts towards higher values of x.

The number of H-bonds broken by one molecule of cosolvent per molecule of water [f/(1-x)] has also been calculated (see figure) showing that for dioxan and acetonitrile its value is constant at about 1.6 over a wide range of composition. The effect does gradually disappear with solvents of increasing basicity.



A linear correlation has been found between the donor number of the solvent and the chemical shift, δ_F, extrapolated for zero content of water in the various systems. The values of δ_F obtained from systems containing both dioxan and DMSO in water indicate that the basicity of the mixed non-electrolyte is always greater than that calculated as an average from the donor numbers and fractional populations of the components.

The estimates of the values of f/(1-x) for DMSO and dioxan in the ternary system show that the presence of the former enhances the interaction of dioxan with water up to x(DMSO)~0.7 in the mixed non-electrolyte but dioxan does not change the capabilities of the more basic partner.

The chemical shift data do not allow us to gain any definite evidence for hydrophobic hydration either in the binary or in the ternary mixtures. [3,5]

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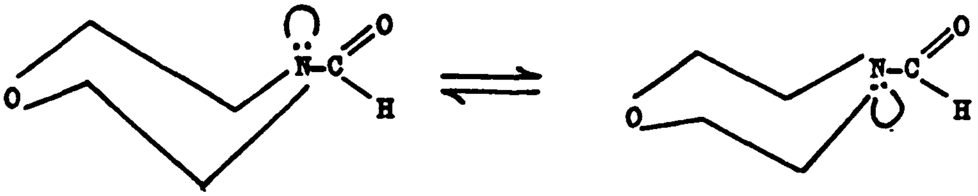
2-5 (P) NUCLEAR MAGNETIC RESONANCE STUDY OF N-METHANOYLMORPHOLINE

Salman R. SALMAN, Akl M. AWWAD and Etamad I. ALLOSE
Petroleum Research Center, Council of Scientific Research,
Jadiriya, P.O. Box 10039, Baghdad, IRAQ

Carbon-13 nmr chemical shifts of N-methanoylmorpholine (NMM) in different solvents indicate that this compound exists in two conformations (1a) and (1b). This compound is used as a selective extractant for monocyclic aromatic hydrocarbons from petroleum feed stocks. Therefore, we studied the interaction of NMM, dissolved in chloroform, with water, methanol, benzene, toluene, o-xylene, p-xylene and mesitylene. The proton chemical shift of the aldehydic proton of NMM was used as a probe for the interaction of NMM (in chloroform), with the above molecules.



(1a) **(1b)**

Water and methanol interact with NMM (in chloroform) through a hydrogen bonding mechanism, in which water forms a cage round the NMM molecules.

NMM interacts with the aromatic compounds, in the presence of chloroform, through a charge-transfer mechanism. The interaction decreases in the following order

toluene > benzene > m-xylene > p-xylene > o-xylene > mesitylene.

2-6 (P) AB INITIO CALCULATIONS OF THE HYDRATION OF AMIDES

A.J. GRANT, T.H. LILLEY and B.T. PICKUP
Chemistry Department, The University, Sheffield, S3 7HF, ENGLAND

Experimental studies of the behaviour of amino acids. peptides and derivatives of these have occupied our attention for some time. Most of the work presented to date has been concerned with the interactive behaviour of such solutes in water although more recently some aspects of their solvation have been considered. The work to be presented represents the first stage of a study which ultimately should lead to a Molecular Dynamics approach to the solvation of peptides.

Ab initio calculations of the energetics of hydration of the two amides, formamide and N-methylacetamide, have been performed. In particular, we have explored the potential surfaces in the regions corresponding to carbonyl group - water and amino group - water hydrogen-bonding interactions. Information will be presented on these surfaces and also the perturbations induced in the solvation behaviour of the H-bond donor in the amide group by the solvation of the H-bond acceptor in the group will be delineated.

The information presented relates directly to several major problems in protein chemistry and in particular to the heat capacity behaviour of the amide group and the "binding" of water to protein surfaces.

2-7 (P) STUDY ON THE INTERACTION PROPERTIES OF AMIDES CONTAINING THE NH-GROUP

P. RUOSTESUO, S. KAARTINEN, V. RUKAJÄRVI, P. PIRILÄ and
L. HEIKKINEN
Department of Chemistry, University of Oulu, SF-90570 Oulu,
FINLAND

The self-association of amides containing the NH group (e.g. 2-pyrrolidinone and N-monosubstituted sulfur amides), is relatively strong according to IR spectroscopic studies. However, the self-association is perturbed in strongly basic solvents. [1,2]

On the other hand, an examination of the thermodynamic excess functions as well as the excess dielectric properties and nmr data of the compounds in different solvents clearly reveals both the solute-solute and the solute-solvent interactions of these amides. Nitrogen-15 and oxygen-17 nmr chemical shifts, as well as NH coupling constants, are quantities which reflect especially well the structure and environment of the amide.

An examination of the chemical shifts of various nuclei of the lactam ring in 2-pyrrolidinone reveals that self-association is perturbed by dimethylsulfoxide, which has basic properties more pronounced than those of the lactams. Furthermore, the excess volumes and also the excess dielectric permittivities are negative for all the 2-pyrrolidinone- and N-methylbenzenesulfonamide - solvent mixtures studied. In addition, the values of the excess dielectric constants decrease with increasing temperature. Considering all of the results, our studies show that both the polarity and the hydrogen-bonding abilities of the components of binary mixtures are well reflected in both dielectric and spectroscopic properties of the amides. [3,4]

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2-8 (P) SPECTROSCOPIC STUDIES OF AMIDE SOLVATION

Martyn C.R. SYMONS and Graham EATON

Department of Chemistry, University of Leicester, Leicester,
LE1 7RM ENGLAND

Fundamental and overtone infrared spectroscopy has been used to study the solvation of various simple amides in protic/aprotic media.

Primarily the carbonyl stretch of the amide and the hydroxyl overtone (1st and 2nd) bands were used with success. Further the N-H overtone band was monitored.

The results were subjected to curve analysis techniques in order to provide detailed information on the separate species involved.

2-9 (P) IONIC ASSOCIATION OF NH_4SCN IN DIMETHYLFORMAMIDE AND IN TETRAHYDROFURAN

J. RANNOU and M. CHABANEL
Laboratoire de Spectrochimie des Ions UER de Chimie, 2, rue de la Houssinière - 44072 Nantes Cedex, FRANCE

The ionic association of NH_4SCN in dimethylformamide (DMF) and in tetrahydrofuran (THF) solutions has been investigated by infra-red spectroscopy. The association behaviour of NH_4SCN is roughly the same as for alkali thiocyanate solutions. However, the ν (CN) frequency of SCN^- in DMF (2056 cm^{-1}) is completely insensitive to ion pairing, which has to be studied in the ν (CS) and δ (SCN) regions. This equilibrium is nearly athermic and entropy-controlled. In THF, the association is more pronounced and two species are observed beyond the ion pair at 2049 cm^{-1}: a quadrupole (2026 cm^{-1}) and probably a triple ion (2069 cm^{-1}).

The association of SCN^- with NHR_3^+ occurs to a lesser extent than with NH_4^+, even though frequency shifts are larger. The hydrogen bonding of SCN^- with hexafluropropan-2-ol and with 4-chlorophenol is similar to its association with NH_4^+ or NHR_3^+.

2-10(P) ON THE STRUCTURES OF THE NEUTRAL MERCURY(II)HALIDES IN SOLUTION, AND THE COORDINATION PROPERTIES OF SOME SOLVENTS

M. SANDSTRÖM, I. PERSSON, P.L. GOGGIN
Department of Inorg. Chemistry, Royal Institute of Technology,
S-100 44 Stockholm, SWEDEN

Raman and infrared spectra of the stretching frequencies of mercury(II) halides in a range of solvents have been recorded and combined with literature data. The frequencies decrease as the interaction of the solvent with the HgX_2 entity increases. Correlations with the dipole moment of the solvent can be made within specific groups of solvents with similar donor atoms.

The structures of the solvated HgX_2 molecules have been determined by large-angle X-ray diffraction methods in pyridine, tetrahydrothiophene and DMSO solutions, and a semi-empirical correlation of the XHgX angle and the frequency shift is made.

The donor numbers proposed by V. Gutmann, based on enthalpy measurements of the adduct formation $SbCl_5 \cdot L$ (L = solvent molecule) in 1,2-dichloroethane solution, are compared with the Sb-Cl stretching frequency of the adduct in solution. An alternative relative scale of the donor strength of the solvents, derived from the frequency shifts of the stretching frequencies of the $HgBr_2$ molecule in solution, is proposed.

2-11(P) IONIZATION EQUILIBRIA OF $CoCl_2$ AND $CoBr_2$ IN DMF SOLUTIONS

M. PILARCZYK, W. GRZYBKOWSKI and L. KLINSZPORN
Department of Physical Chemistry, Technical University of Gdańsk,
80-952 Gdańsk, POLAND

The cobalt(II) halides dissolved in N,N-dimethylformamide (DMF) exhibit a variety of electrolytic behaviour, as shown by their molar conductance curves. Visible absorption spectra of the $CoCl_2$ and $CoBr_2$ in DMF solutions as well as the spectra of the mixed solutions of $Co(ClO_4)_2$ + Et_4NX have been determined and were analyzed in terms of the nature of the ionization equilibria involved. The results indicate that formation of the complex electrolytes $[Co(DMF)_6^{2+}]$ $[CoCl_3DMF^-]_2$ and $[CoBr(DMF)_5^+]$ $[CoBr_3DMF^-]$, is responsible for the electrolytic properties of the respective solutions. The formation constants of the chloro- and bromo-complexes of cobalt(II) are derived.

2-12(P) MIXED METAL COMPLEXES IN SOLUTION. SPECTROSCOPIC AND THERMODYNAMIC INVESTIGATION OF HETEROBINUCLEAR METAL(II) - CITRATE COMPLEXES

Raffaele BONOMO[a], Pier G. DANIELE[b], Allesandro DE ROBERTIS[c], Giorgio OSTACOLI[b], Enrico RIZZARELLI[a] and Silvio SAMMARTANO[c]
[a]*Dipartimento di Scienze Chimiche dell'Universita, viale A. Doria 6, 95125 Catania, ITALY*
[b]*Dipartimento di Chimica Analitica dell'Universita, via G. Bidone 36, 10125 Torino, ITALY*
[c]*Istituto di Chimica Analitica dell'Universita, via dei Verdi, 98100 Messina, ITALY*

Heteronuclear complexes have been comparatively little studied, probably because of the difficulty in identifying accurately the complex species formed in solution. Most of these studies are concerned with mixed metal complexes of hydroxypolycarboxylic acids with a variety of metal ions. These reports do not include any determination of the stability constants for these complexes. [1,2] Recently, some of us have demonstrated that mixed metal complexes are formed for the systems: copper(II) citrate + other divalent cations, and have determined the relative formation constants [3,4].

To obtain a better understanding of the forces leading to the formation of a heteronuclear species and to identify the influences that metal ions exert on each other, we carried out spectrophotometric and e.s.r. measurements on mixed metal complexes of copper(II) citrate with diamagnetic divalent cations.

The experimental results provide useful information, with structural implications on the formation of such chelates. The comparison between $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ changes pertinent to the citrate homobinuclear complexes and those concerning the citrate heterobinuclear species permit us to draw some conclusions about the reasons for the higher stability of mixed metal complexes with respect to the parent simple species.

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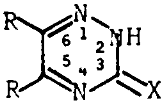
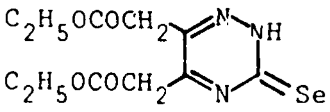
2-13(P) EFFECT OF SOLVENT POLARITY ON THE TAUTOMERIC EQUILIBRIUM AND SPECTRAL PROPERTIES OF 5,6-DIETHOXYCARBONYLMETHYL-3-SELENO-1,2,4-TRIAZINE (SeTEK)

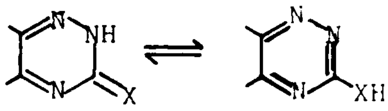
Joanna MASLOWSKA and Jadwiga JAROSZYNSKA
Institute of General Food Chemistry, Technical University of Łódź, 90-924 Łódź, POLAND

Derivatives of 1,2,4-triazine (I) can be considered to be cyclic (oxy, thio or seleno-) semicarbazones of α-diketones. The present paper contains the results of UV spectral investigations on 5,6-diethoxycarbonylmethyl-3-seleno-1,2,4-triazine (SeTEK) (II). The following solvents were used: cyclohexane, 1,4-dioxane, isopropanol, methanol, 98% ethanol and water. The spectra of SeTEK show two characteristic bands at 35000 and 32000 cm^{-1}. The absorption coefficients of both must be associated with the transition $\pi \longrightarrow \pi^*$. [1] To find the precise positions of both these bands, as well as of other possible bands, the method of spectrum differentiation was used. [2] The data allow us to assume that the transition $n \longrightarrow \pi^*$, in methanol solution, takes place at about 27000 cm^{-1}.


I

X=O,S or Se


II


III IV

This compound in solution reveals the same properties as those of its sulphur analogue (TTEK), i.e. both compounds exist in two tautomeric forms and that the dielectric constant of the solvent is a factor determining the position of tautomeric equilibrium. Solvents of higher polarity shift the equilibrium (III) $\rightleftharpoons$ (IV) to the right, bringing about an increase in the content of the form with an -SeH or -SH group respectively.

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2-14(P) SPECTRAL STUDIES ON SOME PYRIMIDINE DERIVATIVES

A.A. HASANEIN and M.A.M. MORSI
Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, EGYPT

The electronic absorption spectra of 5-chlorouracil, 5-bromouracil, 5-iodouracil, 5-bromocytosine and 5-iodocytosine have been measured in a series of twenty different solvents. The solvent effects on the spectra have been discussed and the solvent-induced spectral shifts have been analysed in relation to different solute-solvent interaction mechanisms using a regression technique.

2-15(P) MIXED LITHIUM HALIDE-LITHIUM THIOCYANATE AGGREGATES IN WEAKLY POLAR SOLVENTS

P. GORALSKI(1) and M. CHABANEL
Laboratoire de Spectrochimie des Ions UER de Chimie, 2, rue
de la Houssinière - 44 Nantes, FRANCE
(1)*on leave from the Department of Physical Chemistry,*
Institute of Chemistry, University of Lodz, POLAND

The SCN^- ion is a valuable spectroscopic probe for investigating ionic aggregates in solutions. Mixed aggregates between LiSCN and LiX (X = Cl, Br, I) have been studied by IR spectroscopy in weakly polar solvents (ketones, esters, carbonates, tetrahydrofuran, ethers) where LiSCN is know to be more or less aggregated. The stoichiometry of these aggregates has been determined by JOB's method.

When X = Cl or Br, mixed dimers Li_2XNCS are formed in all cases except in ethers. The frequency shift of $\nu(CN)$ ($\sim$ 2040 cm^{-1}) in mixed dimers relative to $(LiNCS)_2$ is positive ($\Delta\nu$ = +8 cm^{-1} in Li_2ClNCS and +4 cm^{-1} in Li_2BrNCS). It is due in part to the removal of the mechanical coupling between both SCN groups in $(LiNCS)_2$ but also to small changes in the lithium-thiocyanate bonding. In THF the dimer stability increases in the order $(LiNCS)_2 < Li_2ClNCS < (LiCl)_2$ and the enthalpies of formation from the ion pairs are in the order $(LiNCS)_2 > Li_2ClNCS$ as expected.

In ethers LiBr is known to be tetramerized and LiNCS dimerized. In LiBr-LiSCN mixtures, small amounts of Li_4Br_3NCS are formed with a $\nu(CN)$ frequency at 2003 cm^{-1} instead of 1992 cm^{-1} for $(LiNCS)_2$. Mixed aggregates between LiI and LiNCS seem to be less stable than other mixed aggregates. However, in sterically-hindered ethers various new IR bands close to 2000 cm^{-1} are probably due to mixed tetramers $Li_4I_p(NCS)_{4-p}$.

2-16(P) HIGH PRESSURE OXYGEN-17 NMR STUDY OF THE WATER EXCHANGE ON THE LOW SPIN Ru^{3+} AND Ru^{2+} IONS.

L. HELM, I. RAPAPORT, and A.E. MERBACH[a], P. BERNHARD and A. LUDI[b]
a) *Institut de Chimie Minérale et Analytique, UNI-Lausanne,*
CH-1005 Lausanne, SWITZERLAND

b) *Institut für Anorganische Chemie, UNI-Bern, CH-3012, Bern,*
SWITZERLAND

Water-exchange studies on diamagnetic trivalent hexaaquametal ions of variable ionic radii, and on di- and trivalent first row high spin transition metal ions have shown that two factors can explain the associative/dissociative character of the mechanism of these reactions: the extent of dissociative character increases with the filling of the d orbitals, but decreases with the increase in ionic radius. For the ruthenium ions the prediction is not obvious: their relatively small ionic radii and their filled t_{2g} orbitals favor a dissociative activation mode, but the fact to belong to the second row transition metal ions favors an associative activation mode.[1]

The relatively slow water exchanges on Ru^{3+} and Ru^{2+} were studied by isotopic labelling technique, using ^{17}O-NMR to follow the progress of the reactions. This study was performed as a function of temperature and pressure (up to 225 MPa), as well as acid concentration in the case of Ru^{3+}, to take into account the exchange pathway involving the $Ru(H_2O)_5(OH)^{2+}$ species ($k_{obs} = k_1 + k_2/[H^+]$). The results are the following:

	k^{298}	ΔH*m jHn^{-1}	ΔS*, $JK^{-1}m^{-1}$	ΔV*, cm^3m^{-1}
$Ru(H_2O)_6^{3+}$	$3.5\cdot10^{-6}\ s^{-1}$	90 ± 4	-48 ± 14	-8.3 ± 2.1
$Ru(H_2O)_5(OH)^{2+}$	$1.1\cdot10^{-6}\ ms^{-1}$	137 ± 6	+101 ± 18	-2.1 ± 1.4
$Ru(H_2O)_6^{2+}$	$1.8\cdot10^{-2}\ s^{-1}$	88 ± 10	+17 ± 33	-0.4 ± 0.7

This leads us to the assignement of an I_a mechanism for water exchange on $Ru(H_2O)_6^{3+}$, where as for $Ru(H_2O)_5(OH)^{2+}$ and for $Ru(H_2O)_6^{2+}$ the exchanges take place through pure interchange I mechanisms.

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3-1 (P) SOLUTION EQUILIBRIA OF METAL COMPLEXES OF o-PHENYLENEDIAMINE-TETRAACETIC ACID AS VIEWED FROM THEIR THERMODYNAMIC PARAMETERS AND CRYSTAL STRUCTURES

N. NAKASUKA, S. AZUMA, K. MATSUMURA and M. TANAKA
Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, JAPAN

Calorimetric and potentiometric studies have given thermodynamic parameters for the protonation of o-phenylenediamine-N,N,N',N'-tetraacetic acid (PhDTA, H_4L) and its complexation with several divalent metals in aqueous solutions ($25^{\circ}C$, $I = 1$ mol dm^{-3} ($NaClO_4$)). [1]

Heats of protonation of this ligand are greatly reduced at the nitrogen atoms in comparison with EDTA and CyDTA, and the second protonation is even endothermic ($-\Delta H_1 = 4.7$, $-\Delta H_2 = -2.8$ kJ mol^{-1}). Hence $-\Delta H(ML)$ is always more negative for PhDTA than for the last two ligands for the same metal ion, and an endothermic complex formation was observed for cobalt and zinc. The variation in enthalpy of complexation of PhDTA with metal ions is roughly parallel to that for the other two ligands. On the other hand, the entropy of complexation, $\Delta S(ML)$, is practically identical to that of EDTA for a given metal. Consequently the complex formation is entropy-driven for PhDTA more markedly than for EDTA.

Thermodynamic parameters for a reaction ($ML + H \rightleftharpoons MHL$) may be classified into two categories: (a) Smaller or even negative $-\Delta H$ and larger ΔS, for Mn, Cd, Hg and Pb with larger ionic radii. These values are similar to those for protonation of the carboxylate oxygens, O_c, of PhDTA itself. Thus protonation may occur on an O_c not bound to the central ion. (b) Larger enthalpy and smaller entropy for Co, Ni, Cu and Zn. In this case the formation of a protonated MHL should include the bond-rupture of $M\text{-}O_c$, followed by hydration to a metal ion (M).

Some evidence from a crystallographic investigation is in line with the above consideration : A central metal ion is hexacoordinate in ZnH_2Lw_2, K_2ZnLw_3 and Na_2CuLw_4 ($w:H_2O$), while Mn is heptacoordinate in Mn_2Lw_6, and Cd is octacoordinate in Cd_2Lw_8. The dinuclear complex contains an MnO_6 or a CdO_7 polyhedron.

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3-2 (P) EQUILIBRIA IN ACETONE MEDIUM. XIII.COBALT(II) - TRIPHENYLPHOSPHINE OXIDE COMPLEXES: A MANIFESTATION OF THE SYMBIOTIC EFFECT

M. MOLINA, Marcia H.M. PACCIULLIO and C. MELIOS
Departamento de Quimica Analitica, Instituto de Quimica, UNESP,
C.P. 174, Araraquara, 14.800, BRAZIL

The present communication deals with the $Co(ClO_4)_2$-triphenylphosphine oxide (tppo) system, investigated at 25 °C in acetone(ac) solution in which $Co(ClO_4)_2$ behaves as a strong electrolyte with an absorption spectrum characteristic of octahedral Co(II). The successive and overall stability constants (K_n and β_n, respectively) were determined as described previously.[1] The body of experimental evidence indicates that mononuclear Co(II)-tppo complexes with stoichiometries ranging from 1:1 to 1:5 are formed. The species comprising up to two tppo exist in both tetrahedral and octahedral configurations: $[Co(tppo)(ac)_5]^{2+}$, $[Co(tppo)\ (ac)_3]^{2+}$($K_1=K_1^{oct}+K_1^{tet}=570$). $[Co(tppo)_2(ac)_4]^{2+}$, $[Co(tppo)_2(ac)_2]^{2+}$($K_2=K_2^{oct}+K_2^{tet}=363$). The remaining species are tetrahedral: $[Co(tppo)_3ac]^{2}$ ($\beta_3=1.3x10^7$), $[Co(tppo)_4]^{2+}$ ($\beta_4=1.4x10^9$) and $[Co(tppo)_4]^{2+}$.tppo ($\beta_5=2.0x10^{11}$); in the last complex one molecule of tppo is not directly bound to Co(II). These results, in connection with those previously found for the $CoCl_2$-tppo system,[1] ($\beta_1=1.40x10^4$; $\beta_2=6.77x10^6$; $\beta_3=1.77x10^9$; all species have tetrahedral configuration, including $CoCl_2$; the metal salt and the complex species formed in solution are almost undissociated; the third complex corresponds to the ion-pair $[CoCl(tppo)_3^+.Cl^-]$), clearly indicate that tppo forms markedly more stable complexes with $CoCl_2$ than with Co(II); this is not readily understood in the light of simple theoretical considerations. The reported results are tentatively rationalized by taking into account the "symbiotic effect"[2]: once the ion Co(II) has been coordinated by the hard ligand Cl^- it becomes a hard Lewis acid and hence the $CoCl_2$ affinity for the hard ligand tppo is considerably enhanced relative to Co(II).

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3-3 (P) CORRELATION OF ACIDITY OF PHENOL AND BUTENONE DERIVATIVES WITH SOLVENT PROPERTIES.

S.EL KADRY, O. DABBIT and S. WASIF
Department of Chemistry, Faculty of Science, Aleppo University, Aleppo, SYRIA.

The acidic properties of butenone derivatives were investigated in protic and aprotic solvents. The pK_a data agree well with extrapolated values obtained from a separate study of the same acids in water-organic solvents mixtures.

The correlation of pK_a data with solvent properties such as donor and acceptor numbers, dielectric constants and solvent self-ionisation constants, pK_s, revealed a distinct difference between protic(H_2O, MeOH, EtOH and i-PrOH) and aprotic (DMSO, DMF and acetone) solvents. Aprotic solvents fall in the order DMSO > DMF > acetone which is identical with the charge density on the oxygen atom.

Solvent-solvent and solvent-solute interactions exist in such media to differing extents which could partly account for the observed differences in acidic behaviour.

3-4 (P) SELECTIVE SOLVATION OF SILVER(I) SALTS IN WATER-PYRIDINE MIXTURES

C. KALIDAS and A. PALANIVEL
Department of Chemistry, Indian Institute of Technology,
Madras-600 036, INDIA

Selective solvation of ions in mixed solvents influences many chemical phenomena such as solubilities, rates of chemical reactions and phase-separation phenomena. [1] It also has potential technological value. [2] The present investigation deals with the study of selective solvation of Ag(I) sulphate, bromate and iodate in water-pyridine (Py) mixtures by determination of Gibbs energies of transfer of the concerned ions and solvent transport number measurements. Salt solubilities combined with a suitable extrathermodynamic assumption (nLJP method) and a concentration cell with transference proposed by Wagner [3] were employed for this purpose. The Gibbs energy of transfer of silver ion continuously decreases with the addition of pyridine while that of the anions increases under the same conditions. The solvent transport number, Δ, of Py for all the salts increases with the addition of Py, passes through a maximum ($\Delta_{max} = 2.9$ at $x_{Py} = 0.55$ for Ag_2SO_4, $\Delta_{max} = 9.0$ at $x_{Py} = 0.45$ for $AgBrO_3$ and $\Delta_{max} = 5.0$ at $x_{Py} = 0.45$ for $AgIO_3$) and then decreases. These results indicate a heteroselective solvation of all the salts in these mixtures.

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3-5 (P) THE METHANOLYSIS OF *t*-BuI

Raquel M.C. GONÇALVES and Filomena E.L. MARTINS

Centro de Electroquímica e Cinética da Universidade de Lisboa,
Instituto Bento da Rocha Cabral 14, 1200 Lisboa, PORTUGAL

The solvolytic reaction of *t*-BuI in MeOH was studied under the experimental conditions $[t\text{-BuI}] = 0.01$ mol dm^{-3}, P = 1 atm over the temperature range 20 to 50 $^{\circ}$C.

t-BuI in MeOH has a well-defined absorption band [1] which allows one to follow the decrease in reagent concentration, during the solvolytic reaction, by UV spectroscopy. On the other hand, a conventional conductance technique can be used to measure the increase in concentration of the product. In addition, *t*-BuI undergoes thermal (> - 5°C) and photochemical decompositon.[2]

During this work several aims were achieved:

(i) to identify the decomposition products of *t*-BuI,
(ii) to determine the rate constants of the solvolytic reaction by the two techniques,
(iii) to verify how the rate constants were affected by *t*-BuI decomposition,
(iv) to calculate thermodynamic functions of activation and
(v) to discuss different mechanistic hypotheses. [2,3]

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3-6 (P) CORRELATION ANALYSIS OF SOLVENT EFFECTS ON SOLVOLYSIS OF *t*-BUTYL HALIDES

Lidia M.P.C. ALBUQUERQUE, Ana C.O.L. FIGUEIRA, Cristina R. R. OLIVEIRA
Centro de Electroquímica e Cinética da Universidade de Lisboa,
Instituto Bento da Rocha Cabral 14 - 1200 Lisboa, PORTUGAL.

The first systematic studies of solvent effects on the rates of chemical reactions were done more than a century ago. The development of correlation analysis in this area has been a slow process but has recently been more popular. However, there are still basic difficulties arising from the superficial knowledge of the role of the solvent, the appropriate choice of the process model and suitable statistical evaluation methods [1,2].

Our aim is to discuss, both qualitatively and quantitatively, the different solute-solvent interactions, based on the effect of moderate changes of the solvent or substract on kinetic parameters. To perform the correlation analysis, the solvolytic reactions of *t*-butyl halides in various polyalcohols were studied at 25 °C (Table 1), and the specific rate constants were correlated with selected empirical solvent parameters.

Solvent effects on reactivity were interpreted in terms of the different solvation susceptibility of initial and transition states. Multiparametric equations consisting of linear combinations of the available empirical parameters were used. The statistical analysis was performed using simple and multiple linear regressions.

Table 1 - Specific rate constants, $k.10^6/s^{-1}$ t=25C

substract / solvent	Bu^tCl	Bu^tBr	Bu^tI
1,2-Ethanediol	24,26	956,1	2806
1,2-Propanediol	3,115	93,31	276,0
1,3-Propanediol	4,660	318,2	------
1,2-Butanediol	0,7268	26,68	70,03
1,3-Butanediol	1,021	31,16	89,89
1,4-Butanediol	1,118	48,87	155,0
2,3-Butanediol	0,5781	13,30	32,79
Diethyleneglycol	2,056	143,2	684,6
Triethyleneglycol	0,8518	72,27	500,8

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3-7 (P) MEDIUM EFFECT IN THE ELECTROREDUCTION OF NITROMESITILENE

Andrzej KAPTURKIEWICZ and Marcin OPALLO
Institute of Physical Chemistry of the Polish Academy of Sciences
01-224 Warszawa, Kasprzaka 44/52 POLAND

One-electron reduction of nitromesitilene to the corresponding radical anion has been studied at a hanging mercury drop electrode in various perchlorate salt solutions in five organic solvents: dimethylsulfoxide, dimethylacetamide, propylene carbonate, hexamethylphosphortriamide and N-methylformamide. Standard redox potentials, diffusion coefficients, standard rate constants and transfer coefficients have been evaluated using cyclic voltammetry measurements. The results obtained are compared with literature data for dimethylformamide and acetonitrile solutions.

The standard rate constants were found to depend on the cation of the supporting electrolyte as well as the solvent. It is shown that the rate constants (corrected for both ion-pair formation and the double layer effect) cannot be described by classical theories of heterogeneous electron transfer. It is shown that the dielectric dynamic properties of the solvent, described by the dielectric relaxation time, influence the rate of the heterogeneous charge transfer; the greater the dielectric relaxation time of the solvent the smaller the reaction rate.

3-8 (P) MUTUAL INFLUENCES OF IRON(III), CHROMIUM(III) AND THE ELEMENTS OF THE SCANDIUM SUBGROUP ON COMPLEXATION IN AQUEOUS SOLUTIONS

A.E. BAEV, T.L. ZALEVSKAYA, O.N. CHUDNOVSKAYA, E.V. RADION
Byelorussian Technological Institute, 220630, Minsk,
Sverdlova 13A, U.S.S.R.

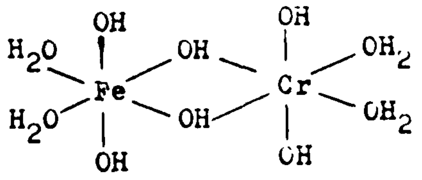
Complexation of iron(III), chromium(III) and the elements of the scandium subgroup by the hydroxyl group, as well as the influence of Cr, Sc, Y, La on the complexation of iron(III) in aqueous solutions over a wide pH-range have been investigated. The experiments have been conducted at a concentration of 10^{-2} M and a temperature of 22±1 °C.

Methods such as dialysis, infra-red spectroscopy, high-frequency conductometry, potentiometry, differential thermography and ion exchange have been used.

The influence of Cr, Sc, Y, La on the complexation of iron in aqueous solutions has been established. The formation of mixed polynuclear hydroxoforms of iron(III) with the ions mentioned has been shown. The tendency to such an interaction reduces in the sequence Cr>Sc>Y>La.

The hydroxyl complexation of Fe-Cr mixtures has been studied in the pH-range 1.5-9.0. At equal concentrations of Fe and Cr of 10^{-2} M and at pH 3, a heteropolynuclear hydroxocomplex with a 1:1 ratio of metals in it exists in the system.

Solid phases are formed between pH 7 and 9. The composition of these phases obtained from the solutions corresponds to the chemical formula $FeCrO_3(OH)_6 \cdot 4H_2O$. Using differential thermography and infra-red spectroscopy it has been established that the compound obtained is a heteropolynuclear hydroxocomplex with structure



3-9 (P) ACTIVATION VOLUMES OF MENSCHUTKIN REACTIONS IN DIFFERENT ALCOHOLS

César A.N. VIANA and António R.T. CALADO
Centro de Electroquímica e Cinética da Universidade de Lisboa
- Instituto Bento da Rocha Cabral - 1200 Lisboa, PORTUGAL

Different thermodynamic parameters of activation have been used to account for the involvement of the solvent in the activated states of reactions in solution.

For many years, the pseudo-thermodynamic parameters which are derived from the temperature coefficients of the rate constants have been determined to compare the solvation properties of the same reaction in different solvents. Such parameters concerned with ionogenic unimolecular reactions in different alcohols and water at different temperatures and pressures have been reported by us over the last fifteen years.

This communication is related to solvent effects on the rate constants of the following MENSCHUTKIN reaction

$$N(C_2H_5)_3 + C_2H_5I \rightarrow (C_2H_5)_4N^+ + I^-$$

in different mono-alcohols. Temperature and pressure coefficients of the rate constants are reported.

The results show that the solvent effects are very well discriminated by the volumes of activation in contrast to the entropies of activation which are obtained with much lower accuracy and do not show any large difference from solvent to solvent.

4-1 (P) CONDUCTANCE STUDIES OF 1:1 ELECTROLYTES IN TETRAMETHYL UREA

E.M. HANNA
Department of Chemistry, University of Basrah, Basrah, IRAQ

In the present investigation the conductance behaviour of LiI, NaI, KI, RbI, CsI, NH_4I, LiBr, NaBr, NH_4Br and LiCl in tetramethyl urea was studied.

The conductance measurements were performed on solutions in the concentration range $(2 - 36) \times 10^{-4}$ M at 25 ± 0.005 °C. At least two runs were made for each salt using freshly prepared stock solutions.

The experimental data were analysed by numerical methods using a computer program including the conductivity equations of Pitts (1953), Fuoss (1978) and Lee and Wheaton (1978).

The important parameters obtained from these analyses were the limiting molar conductivities, (Λ_o), the association constant (K_A), the association distance (d), and the standard deviation (σ_Λ).

The best-fit values of Λ_o, K_A, and d indicate that:-

(1) cations are solvated and the degree of solvation decreases with increasing ion size $Li^+ > Na^+ > K^+ \simeq NH_4^+ > Rb^+ > Cs^+$.

(2) anions are at best weakly solvated.

The behaviour of some sparingly soluble electrolytes in tetramethyl urea was also studied, i.e. KBr, RbBr, CsBr, KNO_3 and $RbNO_3$.

The solubility product data show that the solubility of the salt decreases with increasing size of the solvated ions.

4-2 (P) IONIC MOBILITIES IN MIXED ELECTROLYTES: HYDROPHOBIC INTERACTIONS IN WATER-RICH HYDRO-ORGANIC SOLVENTS

M. PERIE, J. PERIE and M. CHEMLA
Laboratoire d'Electrochemie (U.A. 430) Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05, FRANCE

By labelling migrating ions with radioisotopes, we were able to measure ion mobilities in ternary electrolyte mixtures (2 cations and a common anion) in water and water-rich hydro-organic solvents. One of the most interesting features of the method is that it is valid even at very low ionic concentrations. As a consequence, it allows reliable trace mobility measurements to be carried out, giving access to the maximum structural effect on ionic mobility.

Previous results concerning mixtures of $AgNO_3$ with hydrophilic alkali nitrates$^{(1)}$ have emphasized the necessity of taking the solvent structure properly into account when interpreting the observed "mixture effects". In the present work, the same kind of investigations have been extended to chloride mixtures involving the bulky hydrophobic Ph_4P^+ cation, the electric transport properties of which have never been studied in spite of its biological interest.

New results are presented concerning the concentration dependence of the Ph_4P^+ mobility in its binary salt Ph_4PCl and in ternary mixtures Ph_4P^+-Na^+Cl^- at $I = 0.5$ mole l^{-1}. Three solvents have been investigated: water, water 95 mol% - dimethylsulfoxide 5 mol%, water 95 mol% - acetonitrile 5 mol%. Very large and unexpected "mixture effects" have been observed which may provide new insights concerning the dependence of the hydrophobic ion mobility on solvent composition and ion-ion interaction.

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4-3 (P) INFLUENCE OF THE CO-SOLVENT CONTENTS ON TRANSFERENCE NUMBERS FOR LiBr IN ETHANOL-WATER MIXTURES AT 25°C

Miguel A. ESTESO , Miguel ESPARZA and Domingo M. GRANDOSO

Physical Chemistry Department, Faculty of Chemistry, University of La Laguna, Tenerife, SPAIN

Knowledge of the individual properties of the ions present is necessary in order to study the structure and properties of electrolytic solutions. For this reason, the measurements of ionic transference numbers is of great interest, since these can be determined directly for each individual ion-constituent without having to adopt arbitrary criteria to obtain them from a property of the electrolyte. From this parameter very valuable information can be obtained about the participation of each ion in the charge transport through the solution and, on the other hand, on the basis of the value of the said parameter, correlations can be attempted both with the structure of the ions themselves and with that of the medium.

The use of mixed aqueous-organic solvents is a common and useful practice in electrochemical laboratories, since the physical properties of the medium can readily be manipulated according to the requirements of each particular case. Our laboratory has been engaged on this work for the past few years, presenting transference number values for different ions in ethanol-water mixtures.

The electrolyte chosen for this work was LiBr that presents a great difference between the superficial charge density of both ions, which must leads to their unequal hydration, thus giving rise to structural hypotheses based on the changes observed in their mobilities. In previous communications by this laboratory, values of transference numbers for LiBr in water [1] and in a 10 wt% ethanol-water mixture [2] were presented. In this one, results for 20 and 40 wt% ethanol-water mixtures are also reported, analyzing the influence on these ionic parameters of both the change of the concentration of LiBr solution at each ethanol-water mixture, and specially of the increase of the ethanol content in the solvent.

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4-4 (P) EQUILIBRIUM RADIAL DISTRIBUTION FUNCTIONS OF BINARY MIXTURES AND ION MOBILITIES AT INFINITE DILUTION

Y.M. KESSLER, R.H. BRATISHKO, R.B. LYALINA, R.S. KUMEEV
*Institute of Non-Aqueous Solution Chemistry of the Acad. of Sci. of
the U.S.S.R., Academicheskaya Street, 1, Ivanovo, 153018, U.S.S.R.*

Consideration is given to the variation of the Walden product with composition, $\Lambda_o\eta = f(x_2)$, of binary mixtures H_2O + L, where L is a dipolar (protic or aprotic) organic cosolvent and x_2 is its mole fraction. A classification scheme of H_2O + L mixtures at small x_2 is advanced to distinguish their structural peculiarities. This is based on the "structural code" $|\frac{a}{b}|$ where a=b=0 if $f(x_2)$ has no maximum and minimum or a=b=1 if there are both extrema. An independent structural characteristic of binary mixtures may be obtained with the use of Kirkwood-Buff integrals over RDF g(r). At $x_2=0$

$$G_{ij}^{o} = 4\pi N_A \int_o^{\infty} [g_{ij}(r)-1]r^2 dr = R_{ij} + A_{ij}$$

where R is the repulsive and A is the attractive contribution (positive numerical values of R and A mean repulsion). Values of R were computed from the geometrical structure of the molecules and of A from thermodynamic data. Some results are given in Table 1. One can see from the Table that $f(x_2)$ gives 4 different structural groups, in accordance with the characteristics of R_{ij} and A_{ij}. On consideration of Table 1, together with relevant characteristics of molecular motion, we infer ion mobilities are determined to a large extent by ion displacements through short-lived local negative density fluctuations.

Table 1. Structural code $\Lambda_o\eta$(298 K), R_{ij} and A_{ij}(cm^3 mol^{-1},273 K) in H_2O + L

L	Sulfolane	DMF	DMSO	THF	HMPT
LiCl	0 0	1 1	1 1	1 1	0 1
KCL	0 0	0 1	0 1	1 1	0 1
R_{12}	-	188	210	266	396
$-A_{12}$	-	113	141	191	231
R_{22}	-	191	232	302	508
$-A_{22}$	-	79	-236	854	3

4-5 (P) APPRAISAL OF VISCOSITY B COEFFICIENTS FOR THE BROMIDE ION IN DMSO AND HMPT OBTAINED FROM GRAPHICAL EXTRAPOLATION

Kenneth G. LAWRENCE and Antonio SACCO

Department of Chemistry, Birkbeck College, London, ENGLAND
Department of Chemistry, University of Bari, ITALY

Viscosity B coefficients for the series of salts from Pr_4NBr to $Hept_4NBr$ dissolved in dimethyl sulphoxide and hexamethylphosphortriamide have been determined at 25 °C. The B coefficients have been plotted as functions of the tetraalkylammonium cations, and the collinear points extrapolated to obtain ionic B values for the bromide ion. These values are compared with the $B(Br^-)$ values obtained previously using the reference salts Bu_4NBu_4B and Ph_4PPh_4B.

5-1 (P) THERMODYNAMIC PROPERTIES AND SOLUTION EQUILIBRIA OF AQUEOUS DIVALENT TRANSITION METAL ACETATES

Zofia LIBUŚ, Krystyna CHACHULSKA, Teresa SADOWSKA

Department of Physical Chemistry, Technical University of Gdańsk,
80-952 Gdańsk, POLAND

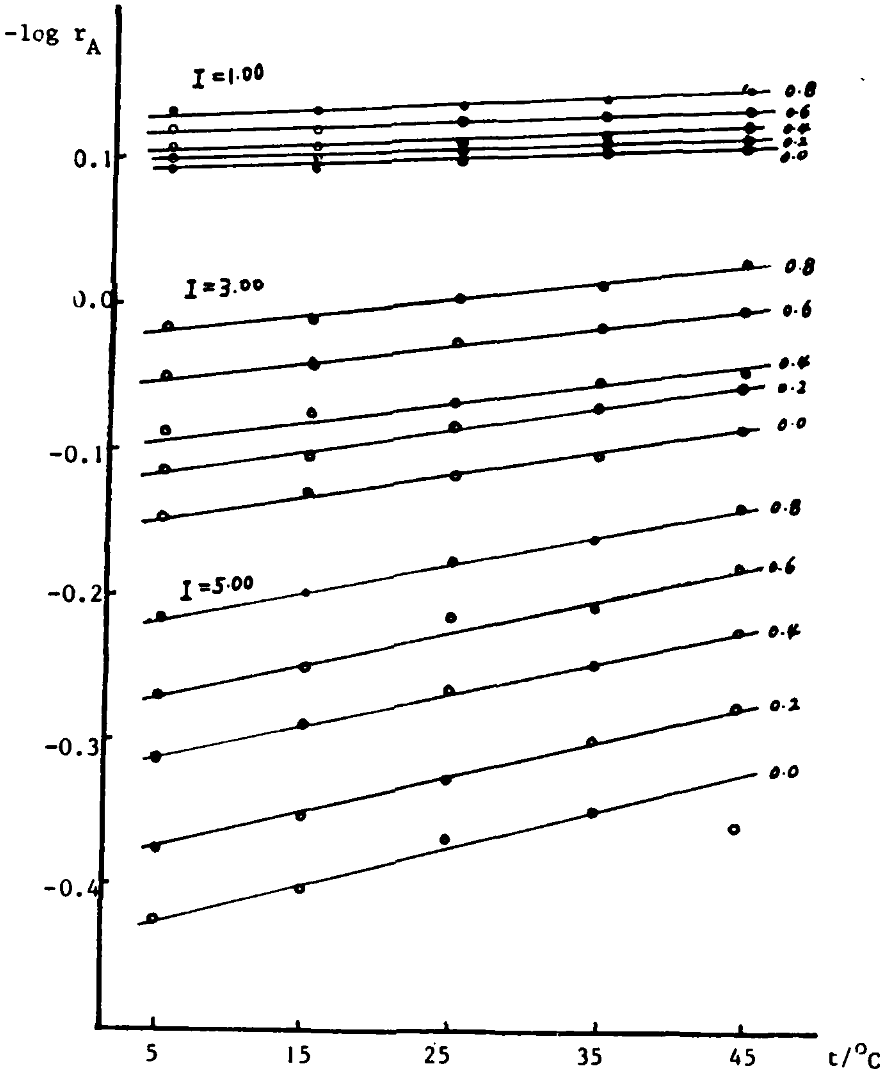
Osmotic coefficients for $Mn(CH_3COO)_2$, $Co(CH_3COO)_2$, $Zn(CH_3COO)_2$, and $Mg(CH_3COO)_2$ in aqueous solution have been determined by the isopiestic method at 25 °C, and the activity coefficients are derived. Changes in the UV and visible absorption spectra induced by changing the concentration have been studied for $Co(CH_3COO)_2$, $Ni(CH_3COO)_2$, and $Cu(CH_3COO)_2$ and are compared with those observed in the mixed solutions of the respective metal perchlorates and CH_3COONa. In order to get information about the influence of the investigated salts on the structure of water, near IR spectra of water in $Mn(CH_3COO)_2$, $Zn(CH_3COO)_2$, and $Mg(CH_3COO)_2$ solutions have been determined.

The results are discussed in terms of coordination and association equilibria of acetate anions with divalent transition metal cations in aqueous solutions.

5-2 (P) THERMODYNAMICS OF MULTICOMPONENT ELECTROLYTE SOLUTIONS THE SYSTEM HCl - $NiCl_2$ - H_2O from 5 to 45 °C

Yang JIA-ZHEN, Liang CHUN-YU, Chu MING-CHEN
Department of Chemistry, Liaoning University, Shenyang, CHINA

This paper reports electromotive force measurements on aqueous mixtures of HCl and $NiCl_2$ at 5, 15, 25, 35 and 45 °C and at six different ionic strengths from 0.5 to 5.0 mol kg^{-1}. The results show that the activity coefficients of HCl obey Harned's rule under the above conditions. The relationship between $\log r_A$ and absolute temperature, T, is expressed by an empirical formula, $\log r_A = a + bT$. The related partial molar enthalpies, L_A, of HCl are proportional to the ionic strength fraction, y_B, of $NiCl_2$ at constant total ionic strength and temperature.



5-3 (P) STUDIES OF ACTIVITY COEFFICIENTS OF MIXED ELECTROLYTES IN MIXED SOLVENTS: SYSTEM OF HCl + NaCl in PrOH + H_2O, at 298.15 K

Chu MING-CHEN, Yang JIA-ZHEN, Liang CHUN-YU, Zheng XI-QUN and Zhu ROE-YAO

Department of Chemistry, Liaoning University, Shenyang, CHINA

This paper reports our studies on HCl + NaCl mixtures in the PrOH + H_2O solvent system by means of emf measurements of the cell without liquid junction:

$$\mathrm{Pt} \mid H_2(1\ \mathrm{atm}) \mid \mathrm{HCl}(m_A), \mathrm{NaCl}(m_B), \mathrm{PrOH}(x), H_2O(1-x) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

at constant total ionic strengths I = 0.1, 0.5, 1.0, 2.0 and 3.0 mol kg^{-1} and at 298.15 K, where m_A and m_B are the molalities of HCl and NaCl, respectively and the mole fraction of PrOH in the mixed solvents, is 0.05.

The results show that HCl approximately follows Harned's Rule from I = 0.1 to 3.0 mol kg^{-1} with correlation coefficients larger than 0.98. Using Harned's expanded equation a slight improvement can be obtained. The Harned interaction coefficients, α_{A1}, decrease as I increases. The trace activity coefficient of HCl and the activity coefficient pure NaCl in the mixed solvents were calculated.

5-4 (P) SOLVATION EQUILIBRIA IN THE SYSTEM: COPPER(II) CATION-SOLVENT-CO-SOLVENT

Andrzej LEWANDOWSKI
Institute of General Chemistry, Technical University of Poznań,
60-965 Poznań, POLAND

The emf of the cell

$$Cu|Cu^{2+}, \text{ solvent A}||Cu^{2+}, \text{ solvent A + co-solvent B}|Cu$$

has been measured for different solvents and used to calculate the free energy of transfer, ΔG_t, of the copper(II) cation from solvent A to its mixture with co-solvent B. It has been found that mixed solvents can be grouped, from the point of view of their solvating properties, as follows:

(i) one component of the mixture preferentially solvates the copper(II) ion:- aqueous mixtures of alcohols and amides [1,2],

(ii) the structure and solvent-co-solvent-solute interactions determine the solvating properties:- aqueous mixtures of sulpholane, dioxan, tetrahydrofuran and acetone,

(iii) mainly the value of the dielectric constant determines the solvating properties:- mixtures of the strong solvator, DMSO, with an electrochemically neutral co-solvent, e.g. a hydrocarbon.

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5-5 (P) EXCESS VOLUMES OF BINARY MIXTURES OF N-METHYLMETHANE- AND N,N-DIMETHYLMETHANESULFINAMIDE WITH CARBON TETRACHLORIDE, 1,4-DIOXANE AND BENZYL ALCOHOL

P. RUOSTESUO, T. MATTILA and S. KURKISUO
Department of Chemistry, University of Oulu, Linnanmaa, SF-90570 Oulu, FINLAND

We have previously presented systematic investigations on the molecular interactions of organic mixtures containing sulfinamide as one component and an alcohol as the other component. [1,2] These IR and nmr spectroscopic studies showed that the interactions of sulfinamide in binary or ternary solution mixtures are of the same order of magnitude as those of carboxamides. [2,3] On the other hand, the behaviour of these amides closely resembles that of the sulfoxides. Since, in our dipole moment and spectroscopic investigations, we have used 1,4-dioxane and carbon tetrachloride as the principal solvents, it was of interest to extend the studies to the thermodynamic excess quantities, such as excess volumes, for binary solution mixtures of sulfinamides and these two solvents.

In the present work, molar excess volumes for mixtures of N-methylmethane- and N,N-dimethylmethanesulfinamide with 1,4-dioxane and carbon tetrachloride have been calculated from experimental density data at four temperatures over the entire composition range. We have also studied mixtures of N,N-dimethylmethanesulfinamide and benzyl alcohol by the same method. The results obtained have been considered in terms of the strength of the molecular interactions in the mixtures.

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5-6 (P) EQUIMOLAR MIXTURES OF TRIVALENT METAL PERCHLORATES AS CONSTANT-IONIC-STRENGTH MEDIA IN STUDIES OF COMPLEX FORMATION IN DIMETHYL-SULPHOXIDE

Danuta PUCHALSKA and Danuta WÓJCIK
Department of Physical Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, POLAND

A new way of accomplishing the constant-ionic-strength medium concept in spectrophotometric studies of complex formation is presented. Equimolar mixtures of trivalent metal perchlorates [Fe(III), Al(III), Ga(III) and In(III)] in dimethylsulphoxide have been used as effectively constant-ionic-strength media for studying the formation of complexes of these metals with the thiocyanate anion. Formation of the complexes has been studied spectrophotometrically and calorimetrically. The complete thermodynamic characteristics, ΔG^o, ΔH^o and ΔS^o, of the complex forming reaction: $M(DMSO)_6^{3+} + SCN^- \rightleftharpoons MSCN(DMSO)_5^{2+}$ have been derived.

5-7 (P) SOLUTE-SOLVENT-SOLUTE INTERACTIONS IN AQUEOUS SOLUTIONS OF SIMPLE CARBOHYDRATES AT 25 °C

G. BARONE, P. CACACE, G. CASTRONUOVO, D. CELOTTO,
P. Del VECCHIO, V. ELIA
Department of Chemistry, University of Naples, via
Mezzocannone 4, I-80134 Naples, ITALY

Recent results from our laboratory are presented concerning the excess thermodynamic properties (free energies, enthalpies and entropies) at 25 °C of aqueous solutions of some monosaccharides and their derivatives. Mixtures of α- and β-methoxypyranosides and of D- and L- enantiomers can help in elucidating the properties of these simple carbohydrates.

The data obtained are compared with other physico-chemical properties and discussed in terms of solute-solvent interactions. Really weak stereospecific interactions are present, so that a chiral recognition between enantiomeric molecules can be demonstrated.

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5-8 (P) A SPECIFIC HYDRATION MODEL FOR THE HOMOTACTIC AND HETEROTACTIC INTERACTIVE BEHAVIOUR OF SOME SACCHARIDES IN WATER

S.H. GAFFNEY, E. HASLAM, T.H. LILLEY and T.R. WARD
Chemistry Department, The University, Sheffield, S3 7HF, ENGLAND

Recently there have been numerous studies on the interaction of saccharides, both single and complex, with the solvent water. Most of the investigations have been directed towards the elucidation of information relevant to the situation in which the solute considered is "infinitely dilute" in the solvent and where solute-solute interactions are absent. Such work is important, but in a biological context of more relevance are the interactions which occur *between* solutes in the solvent. A considerable number of aqueous systems containing saccharides has been investigated, notably by Barone and his co-workers. Most of these have been systems containing only one solute and what we have termed homotactic virial coefficients (i.e. those reflecting like solute - like solute interactions) have been obtained. Rather fewer systems containing two solutes have been studied and there is relatively little information on heterotactic (unlike solute) virial coefficients.

We will present a comprehensive study of the enthalpies of dilution of aqueous solutions containing as solutes the isomeric disaccharides cellobiose, trehelose and maltose solutions containing binary mixtures of these solutes.

The information obtained is combined with earlier results and a specific hydration model is presented which represents rather well the behaviour of a large number of solutes.

5-9 (P) THE ENTHALPY CHANGE OF MIXING OF N-METHYLACETAMIDE WITH OTHER LIQUID AMIDES

A.J. GRANT, T.H. LILLEY and R. SUTTON
Chemistry Department, The University, Sheffield, S3 7HF,
ENGLAND

As part of our programme of work on the behaviour of solutes in N-methylacetamide (NMA) as a solvent we have measured the enthalpy changes on mixing of NMA with the amides formamide, N-methylformamide, N,N-dimethylformamide and N,N-dimethylacetamide. Very marked differences in both the magnitudes and signs of the enthalpy changes are observed for the different mixtures. It is shown that the data can be used to obtain enthalpies of solution and enthalpic virial coefficients. The values obtained for these agree well with the results from independent experimental measurements from our laboratory and independent sources.

The results obtained are discussed in the light of the charge distributions on the molecules obtained from *ab initio* calculations in association with Mulliken population analyses.

5-10(P) SOME ASPECTS OF THE BEHAVIOUR OF SIMPLE AMIDES AND TERMINALLY-SUBSTITUTED AMINO ACIDS IN AQUEOUS, AMIDIC AND MIXED SOLVENTS

G. CONOLE, W. DAVIS, T.E. LESLIE, and T.H. LILLEY
Chemistry Department, The University, Sheffield, S3 7HF, ENGLAND

In recent years we have presented several studies on the behaviour of amino acids, peptides and some of their derivatives in water. Our motivation for pursuing such studies relates particularly to

(i) the tendency of some polypeptides to fold spontaneously into relatively well-defined structures and

(ii) the propensity of peptide substrates to interact with the active sites of some enzymes

In both of the above areas it is clear that the problems involved are both complex and complicated and that the nett energetics of the interactive processes will have many contributions. Some at least of these contributions will be environmentally mediated and if one considers say the first of the above problems, then one can state that in the early stages of protein synthesis, interactions between amino acid subunits will be occurring in an essentially aqueous medium and consequently the nucleation stages of protein folding will be determined to some extent by this medium. However, as folding proceeds, water will be excluded from the interior of globular proteins and the subunits in interior regions will be interacting in an environment which is to a greater or lesser extent amidic in character. The work presented will be particularly directed towards a calorimetric study of the interactions occurring between some simple amides and some terminally-substituted amino acids in water, N-methylacetamide and mixtures of these. It will be shown that the solute-solute interactions depend markedly not only on the nature of the solute but also upon the solvent medium and that there are correlations between the behaviour of the amino acid derivatives in the solvents and some features of protein architecture.

5-11(P) ION-ION INTERACTIONS OF CRYPTATED CATIONS.

N. MOREL-DESROSIERS and J.-P.MOREL
Laboratoire d'Etude des Interactions Solutés-Solvants, U.A. au CNRS n° 434, Université de Clermont II, 63170 Aubière, FRANCE.

Cryptands, such as 222, form very stable inclusive complexes with various metal cations. The properties of the aqueous solutions of these new ionic species may give original information regarding solute-solvent and solute-solute interactions.

The inclusive complex M^+222 is characterized by a quasi-spherical symmetry, a diameter of about 9 Å, and an external hydrophobic shell made up of the CH_2 groups of the ligand, the coordinating heteroatoms being turned towards the inside of the molecular cavity. It has been shown that the cryptated cation is not totally shielded from interactions with the solvent.

Potassium and barium cryptates are of comparable size and differ only in their charge; it is thus particularly interesting to study their ion-ion interactions and to compare them with those of the tetraalkylammonium ions which are considered as typical hydrophobic species.

The heat of dilution measurements show very different results:

- the values obtained for K^+222,Cl^- are comparable to those of Pr_4NCl and Bu_4NCl, showing the hydrophobic interactions of the cryptates.
- the values of $Ba^{2+}222,2Cl^-$ are much smaller than those of potassium cryptate: the strong electrostatic repulsions of the doubly-charged cations oppose the hydrophobic interactions.

The comparison of the ϕ_L *versus* $\sqrt{m}$ curves of the two cryptates studied clearly shows the specific effect of the charge on the interactions of the two hydrophobic species.

5-12(P) COMPLEX FORMATION AND SOLVATION OF $[CuCl_n]^{(2-n)+}$ IN ACETONITRILE, IN N,N-DIMETHYLFORMAMIDE AND IN THEIR MIXTURES

Shin-ichi ISHIGURO, Bojana G. JELIAZKOVA and Hitoshi OHTAKI
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, JAPAN

Equilibria involving the formation of complexes between copper(II) and chloride ions have been studied by calorimetry in acetonitrile (AN), in N,N-dimethylformamide (DMF) and in their mixtures, containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. The formation of copper(II)-DMF solvates has also been investigated in AN. Heats of solution of anhydrous $CuCl_2$ have been measured in the solvents, and enthalpies of solution of the neutral $CuCl_2$ molecule and enthalpies of transfer of Cu^{2+} ions from a reference solvent to others were also determined.

DMF solvates Cu^{2+} stepwise to form $[Cu(DMF)_n]^{2+}$ ($n = 1-4$) in AN in the range of the DMF concentration up to 1 mol dm^{-3} and copper(II) ion is expected to form predominantly $[Cu(DMF)_4]^{2+}$ in all the AN-DMF mixtures with DMF contents of 0.025, 0.05, 0.1 and 0.5 mole fractions. Consequently, the stepwise formation of $[CuCl_n]^{(2-n)+}$ ($n = 1-4$) can be described in terms of replacement of the DMF molecules solvating the metal ion within $[CuCl_{n-1}]^{(3-n)+}$ with chloride ions in each consecutive step.

The stepwise ΔH_1^o and ΔS_1^o in all the mixtures examined were similar to ΔH_1^o and ΔS_1^o in pure DMF, respectively, which suggested the reaction, $Cu(DMF)_4{}^{2+} + Cl^- = CuCl(DMF)_3{}^+ + DMF$. ΔH_4^o and ΔS_4^o in the mixtures were also similar to the respective values in pure DMF, which suggested that the reaction, $CuCl_3(DMF)^- + Cl^- = CuCl_4{}^{2-} + DMF$, occurred, because the existence of unsolvated $[CuCl_4]^{2-}$ has been found by separate experiments. Values of ΔH_2^o and ΔS_2^o increased remarkably, whereas ΔH_3^o and ΔS_3^o decreased remarkably, with a decrease in the DMF content of the mixtures. This indicates that DMF molecules desolvate more extensively in the mixtures of lower DMF content than in those of higher ones. The weaker solvation of $[CuCl_2]$ in the AN-DMF mixtures of a lower DMF content was also confirmed by measurements of enthalpies of solution of the neutral $[CuCl_2]$ complex in the mixtures.

5-13(P) TRANSFER ENTHALPIES OF SOLUTION OF *t*-BuX (X=Cl,Br) AND PARENT COMPOUNDS

Raquel C.M. GONCALVES and Ana M.N. SIMÕES

Centro de Electroquímica e Cinética da Universidade de Lisboa,
Instituto Bento da Rocha Cabral 14, 1200 Lisboa, PORTUGAL

The determination of transfer thermodynamic functions is one of the best methods to study the influence of solvent and substract on the physical-chemical properties of compounds.

The enthalpy of transfer of a particular solute from solvent S_1 to solvent S_2 is obtained by measuring, in a calorimeter, the heat of solution of this solvent in S_1 and in S_2, respectively, at constant pressure.

The following table gives the heats of solution of *t*-BuX in various solvents, as well as the heats of solution of the parent compounds, CX_4 and Me_4NX. The results will be compared, discussed and interpreted in molecular terms.

$\Delta\bar{H}^{o}_{s}$ / J mol^{-1}

SOLVENT	T /°C	SOLUTE Bu^{t}Cl	 Bu^{t}Br	 CCl_4	 $CBr_4$$^{\alpha}$
MeOH	20	1428	1842	-	-
	25	1565	2198	-554	1362
	30	2350	2435	-	-
	35	2653	2840	-	-
	40	3053	3160	-	-
EtOH	20	1301	1330	-	-
	25	1497	1752	-760	1044
	30	1972	2055	-	-
	35	2432	2261	-	-
	40	2711	2703	-	-
Pr^{n}OH	20	1542	1710	-	-
	25	1618	1998	-431	3396
	30	2496	2385	-	-
	35	2862	2787	-	-
	40	3261	2964	-	-
Bu^{n}OH	20	1812	2067	-	-
	25	2103	2366	-198	-
	30	2684	2746	-	-
	35	3015	3002	-	-
	40	3382	3239	-	-
Pe^{n}OH	20	2233	2315	-	-
	25	2560	2629	208	-
	30	2812	3034	-	-
	35	3152	3273	-	-
	40	3534	3587	-	-
Pr^{i}OH	20	3068	3638	-	-
	25	3566	4116	1076	6366
	30	4330	4473	-	-
	35	5119	4771	-	-
	40	5364	5137	-	-
Bu^{t}OH	20	-	-	-	-
	25	6161$^{\beta}$	7217$^{\beta}$	4556$^{\gamma}$	11328$^{\gamma}$
	30	6574	7248	-	-
	35	7158	7299	-	-
	40	7275	7396	-	-

$^{\alpha}$ *Less* ΔH^{o}_{fusion} *= 5020 J mol*$^{-1}$ $^{\beta}$ *extrapolated value* $^{\gamma}$ *at 27°C*

5-14(P) ACIDITY AND HOMOCONJUGATION (BHB^+) OF N-BASES IN CYCLOHEXANONE

Zenon PAWLAK
University of Gdansk, Department of Economics of Production,
81 824 Sopot, POLAND.

From electrometric measurements on protonated N-bases (BH^+) in cyclohexanone the equilibria taken into account are given by eqs. (1) and (2)

$$BH^+ \rightleftharpoons B + H^+ \; ; \; K_a \qquad (1)$$

$$BH^+ + B \rightleftharpoons BHB^+ \; ; \; K_f \qquad (2)$$

The corresponding constants have been calculated using the programme DECFAM [1] which is based on the nonlinear least-squares method.

The homoassociation constants, K_f, obtained are rather small; $\log K_f = 0.9$ to 1.8. Only a few systems were found to associate under experimental conditions, ($C_{BH^+ClO_4^-} = 10^{-3}M$).

The standard deviations of the homoassociation constants are several times greater than those of the corresponding pK_a's. This means that weakly associating systems are not well conditioned and influence of homoassociation on the electromotive force was so small that it was impossible to determine.

The pK_a's of some acid (BH^+) systems must also be considered sceptically because the glass electrode may not work properly.

Most of the acids considered are weaker in cyclohexanone than in acetone [2]; the difference being 1 - 2 pK_a units.

1. J. Kostrowicki, A. Liwo, *Comp. Chem.*, 8, 91 (1984); ibid., 8, 101 (1984).
2. S. Kuna, Z. Pawlak, M. Tusk, *J.Chem. Soc., Faraday Trans. I*, 78, 2685 (1982).

5-15(P) THEORY OF IONIC SOLUTIONS

Arjun J. DANGRE and A.A. DANGRE
Department of Chemistry, University of Poona, PUNE - 411 007, INDIA

The limiting law form of the Debye Hückel theory successfully describes properties of dilute solutions. Using his cluster theory of an imperfect gas, Mayer developed an alternative treatment of electrolyte solutions. This approach is extended in the present work; the dissolved electrolyte is considered to be a dilute ionized gas, while the solvent is taken as a dielectric continuum characterised by a temperature T and a relative permittivity D_o. The derived thermodynamic energy function and the equation of state extend only over the ions in solution. The latter equation gives the osmotic pressure of the ions in solution as a function of concentration and temperature. The large deviations of ionic solutions from ideality are due partly to the large range of the mutual potentials and also to their large values. The pairing of ions or the formation of undissociated molecules even in very dilute solutions is due to the difference in the energy of two oppositely charged ions at large distances in the solvent and at the distance of closest approach of the ionic pairs. In dilute solution in which all ions have charges of the same magnitude, the interaction at short range of all ionic pairs and the effect on this interaction of the long range electrostatic potential of any third ion in their neighbourhood can be accounted for. Very close interactions of triple ions play a negligible role in dilute solutions, so the theory displayed should be moderately satisfactory even beyond the concentrations for which an analytic function could be used.

LIST OF AUTHORS

Abraham M.	3-Sess 2
Ahrland S.	2-17 (0)
Akitt J.W.	2-10 (0)
Alberquerque L.	3-6 (P)
Allose E.I.	2-5 (P)
Amodeo P.	2-4 (0)
Atkinson B.L.	1-4 (0)
Atkinson G.	1-4 (0)
Awwad A.M.	2-5 (P)
Azuma S.	3-1 (P)
Baev A.E.	3-8 (P)
Balk R.W.	3-11 (0)
Barakat A.O.	3-6 (0)
Barczynska J.	4-14 (0)
Barone G.	2-4 (0)
"	5-7 (P)
Barone V.	2-4 (0)
Barthel J.	4-Sess 1
Ben-Naim .	2-19 (0)
Benoit R.L.	3-8 (0)
Bloemendal M.	5-10 (0)
Blandamer M.J.	3-16 (0)
Bonomo R.	2-12 (P)
Boyce J.B.	2-16 (0)
Bratishko R.H.	4-4 (P)
Breen J.	2-3 (P)
Cacace P.	5-7 (P)
Calado A.R.T.	3-9 (P)
Cassol A.	3-9 (0)
Castronuovo G.	5-7 (P)
Celotto D.	5-7 (P)
Chabanel M.	2-9 (P)
"	2-15 (P)
Chadwick I.	5-7 (0)
Chachulska K.	5-1 (P)
Cheek Y.M.	3-7 (0)
Chemla M.	[illegible]-2 (P)
Chen C-T.A.	1-2 (0)
Chin S.	2-8 (0)
Chniber T.	2-13 (0)
Christian S.D.	3-17 (0)
Chun-Yu L.	5-2 (P)
"	5-3 (P)
Claeson T.	2-16 (0)
Clementi E.	2-1 (0)
"	2-8 (0)
"	2-1 (P)
Conole G.	5-10 (P)
Corongiu G.	2-1 (P)
Covington A.K.	2-24 (0)
Craubner H.	5-4 (0)
Cristinziano P.	2-4 (0)
Cummings S.	2-2 (P)
Dabbit O.	3-4 (0)
"	5-8 (0)
"	3-3 (P)
Dangre A.A.	5-15 (P)
Dangre A.J.	5-15 (P)
Daniele P.G.	2-12 (P)
Davis W.	5-10 (P)
Delpuech J.J.	2-13 (0)
Del Vecchio P.	5-7 (P)
Delville A.	2-12 (0)
Detellier C.	2-12 (0)
De Robertis A.	2-12 (P)
Detrich J.	2-1 (P)
Dhabanandana S.	3-1 (0)
Díaz C.	5-7 (0)
Di Bernardo P.	3-9 (0)
Dunn M.	2-14 (0)
Eaton D.R.	2-14 (0)
Eaton G.	2-8 (P)
El [illegible] rakany A.A.	3-6 (0)
El Kadry S.	3-4 (0)
"	5-8 (0)
"	3-3 (P)
Elia V.	5-7 (P)
Elsemongy M.M.	5-6 (0)

END

Telephone (0734) 875123
Ext 7946/7955

THE UNIVERSITY OF READING
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UNIVERSITY OF READING JULY, 15 - 19th, 1985

LATE ABSTRACTS

R.A. Robinson Memorial Lecture, K.H. Khoo, Kuala Lumpur, MALAYSIA
ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTE SOLUTIONS.

2-25(O) IONIC ASSOCIATION OF NH_4SCN IN DIMETHYLFORMAMIDE AND IN TETRAHYDROFURAN
J. Rannou and M. Chabanel, Nantes, FRANCE

3-18(O) COSPHERE-COSPHERE INTERACTIONS IN KINETIC SALT EFFECTS
M.J. Blandamer, J. Burgess, B. Clark, A.W. Hakin, Leicester, ENGLAND
J.B.F.N. Engberts, Groningen, THE NETHERLANDS.

4-16(O) TRANSFERENCE NUMBERS FOR AQUEOUS SOLUTIONS OF SODIUM DODECYLSULFATE WITH AND WITHOUT 1-HEPTANOL
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S. Aduldecha and K. (Indaratna) Kriausakul, Bangkok, THAILAND.

2-17(P) EFFECT OF PRESSURE ON ROTATIONAL ISOMERISM OF CHLOROACETONE IN CARBON DISULFIDE
Y. Taniguchi, S. Sawamura and I. Murakoshi, Kyoto, JAPAN

2-18(P) EFFECT OF PRESSURE ON THE DYNAMICS OF NITRATE ANIONS IN AQUEOUS SOLUTIONS
T. Noguchi, A. Tanaka, K. Suzuki and Y. Taniguchi, Kyoto, JAPAN

2-19(P) EFFECT OF PRESSURE ON THE INTENSITY OF THE ABSORPTION SPECTRA OF ß-CAROTENE AND PYRAZINE IN HEXANE
S. Sawamura, H. Koike. Y. Taniguchi, K. Suzuki, Kyoto, JAPAN

2-17 (P) EFFECT OF PRESSURE ON ROTATIONAL ISOMERISM OF CHLOROACETONE IN CARBON DISULFIDE

Y. TANIGUCHI, S. SAWAMURA, and I. MURAKOSHI
Department of Chemistry, Faculty of Science and Engineering,
Ritsumeikan University, Kita-ku, Kyoto, 603 JAPAN.

The effect of pressure on the conformational equilibrium of chloro-acetone in carbon disulfide has been measured by means of the high pressure infrared spectrum with a diamond anvil cell. at the region of C=O and C-Cl stretching vibrational bands up to 12 kbar. The observed frequencies of the C=O stretching vibration decreased with increasing pressure by -0.56 cm^{-1} kbar^{-1} for the higher frequency bands and -0.47 cm^{-1} kbar^{-1} for the lower bands. The frequencies of C-Cl bands increased by 0.33 cm^{-1} kbar^{-1} for the higher frequency and 0.57 cm^{-1} kbar^{-1} for the lower frequency at 6 kbar. The pressure effects on the frequency shift were discussed with respect to Bauer and Magat's theory of the solvent shift and the intermolecular forces. The volume changes for the transformation from the conformer assigned to the lower frequency to the conformer assigned to the higher have been determined as -1.6 ± 0.1 cm^3 mol^{-1} for C-Cl band and -1.5 ± 0.2 cm^3 mol^{-1} for C=O band. The observed volume changes were considered to be from three theoretical contributions: the intrinsic volume difference between isomers is 0.66 cm^3 mol^{-1}, the packing effect of the solute and solvent is $0 \sim -1.8$ cm^3 mol^{-1}, and the solvent effect is -3.0 cm^3 mol^{-1}. From the pressure dependence of the frequency shifts of the C=O and C-Cl stretching vibrations and the volume changes for the conformational isomerism, it is clarified that the lower frequency bands are assigned to the less polar form and the higher bands to the more polar form.

R.A. ROBINSON MEMORIAL LECTURE

ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTE SOLUTIONS

Kean H. KHOO
Department of Chemistry, University of Malaya, Kuala Lumpur, MALAYSIA.

The limitations of Guggenheim's equations for the activity coefficients of mixed electrolytes are well known. Some examples of these limitations are given. Modern theories of mixed electrolyte solutions may be regarded as building on the Guggenheim treatment by adding terms for binary interactions of ions of the same sign and also ternary interactions involving two ions of one sign and one of opposite sign. The Scatchard treatment probably includes other short-range interactions as well and is very complicated. A simple physical interpretation of the interaction parameters appears to be lacking. The Pitzer treatment offers a more compact and convenient formalism with fewer parameters. These two approaches are outlined and some of the problems associated with their applications are discussed.

2-18 (P) EFFECT OF PRESSURE ON THE DYNAMICS OF NITRATE ANIONS IN AQUEOUS SOLUTIONS

T. NOGUCHI, A. TANAKA, K. SUZUKI, and Y. TANIGUCHI
Department of Chemistry, Faculty of Science and Engineering,
Ritsumeikan University, Kita-ku, Kyoto, 603 JAPAN.

The Raman spectra of the totally symmetric $\nu_1(A_1')$ mode, 1050 cm^{-1} of an NO_3^- ion have been studied in aqueous 2M $LiNO_3$, $NaNO_3$, and KNO_3 solutions at 25 °C up to 2 kbar. The vibrational $G_v(t)$ and rotational $G_r(t)$ correlation functions have been calculated from the Fourier transform of the isotropic and anisotropic Raman profiles at various pressures. The reorientation of the symmetry axis of an NO_3^- ion in the aqueous solutions may be represented by the inertial motion for short times ($t<0.2$ ps) and by rotational diffusion for long times ($t>0.3$ ps). The $G_r(t)$ for the long-time region decays more slowly with increasing pressure, and the decay of $G_r(t)$ does depend upon the cations under pressure. The $G_r(t)$ for the short-time region decays much more slowly than $G_{F.I.}$, the free rotor correlation function for the free NO_3^- ion ($I_{free}=6 \times 10^{-39}$ g cm^2). It does indicate that the rotation of the NO_3^- ion in aqueous solutions is quite restricted. For very short times up to about 0.2 ps at 1 atm, the rotational motion is almost of inertial type with the effective moment of inertia $I_{eff}=20 \times 10^{-39}$ g cm^2. This corresponds to a mean rotation of about 17° of a complex NO_3^- cluster between successive collisions. Under pressure, I_{eff} values increase exponentially for Na^+ and K^+ ($K^+<Na^+$), but for Li^+ we can observe a maximum point at about 1 kbar in the plots of the I_{eff} vs. pressure. On the other hand, we cannot detect any change of the $G_v(t)$ of NO_3^- ion up to 2 kbar at least. In the presentation, we will discuss the dynamic structure of aqueous NO_3^- salt solutions under high pressures.

2-19(P) EFFECT OF PRESSURE ON THE INTENSITY OF THE ABSORPTION SPECTRA OF β-CAROTENE AND PYRAZINE IN HEXANE

Seiji SAWAMURA, Hideki KOIKE, Yoshihiro TANIGUCHI,
Keizo SUZUKI

Department of Chemistry, Faculty of Science and Engineering,
Ritsumeikan University, Kita-ku, Kyoto, JAPAN

The refractive index (n) of a liquid increases on compression; for hexane, n=1.372 under atmospheric pressure but n=1.490 at 640 MPa at 25 °C. Therefore, the pressure effects on the absorption intensity may be compared with the solvent effect such as the Shibuya's equation (1983) including the Chako's one (1934). Solvent effects for the absorption intensity of pyrazine and β-carotene in non-polar solvents have been measured by Myers and Birge (1980). They show that the intensity of pyrazine absorption increases by 3% and that of β-carotene decreases by 9% when the refractive index increases from 1.372 to 1.490. They and Shibuya ascribed this behaviour to a difference in molecular structure, i.e., an spherical molecule for pyrazine and a rod-like one for β-carotene.

We found that the absorption intensity of pyrazine increased by 10% up to 640 MPa, and that of β-carotene decreased by 1.5% up to 200 MPa and then increased by 1.5% up to 640 MPa. A qualitative agreement between the pressure effect up to 200 MPa and the solvent effect, i.e., the enhancement in the absorption intensity of pyrazine and the reduction in that of β-carotene, indicates that the contribution of the refractive index of a solvent to the pressure effect for absorption intensity is not so small. But in the quantitative observation, the enhancement of 10% in the presence effect up to 640 MPa of pyrazine is larger than that of 3% in the corresponding solvent effect, and the situation for β-carotene is the same, i.e., 0%(=-1.5% + 1.5%) in the pressure effect against -9% in the solvent effect, which implies another contribution besides the refractive index in the pressure effect.

2-25(O) IONIC ASSOCIATION OF NH_4SCN IN DIMETHYLFORMAMIDE AND IN TETRAHYDROFURAN

J. RANNOU and M. CHABANEL
*Laboratoire de Spectrochimie des Ions UER de Chimie, 2, rue
de la Houssinière - 44072 Nantes Cedex, FRANCE*

The ionic association of NH_4SCN in dimethylformamide (DMF) and in tetrahydrofuran (THF) solutions has been investigated by infra-red spectroscopy. The association behaviour of NH_4SCN is roughly the same as for alkali thiocyanate solutions. However, the ν (CN) frequency of SCN^- in DMF (2056 cm^{-1}) is completely insensitive to ion pairing, which has to be studied in the ν (CS) and δ (SCN) regions. This equilibrium is nearly athermic and entropy-controlled. In THF, the association is more pronounced and two species are observed beyond the ion pair at 2049 cm^{-1}: a quadrupole (2026 cm^{-1}) and probably a triple ion (2069 cm^{-1}).

The association of SCN^- with NHR_3^+ occurs to a lesser extent than with NH_4^+, even though frequency shifts are larger. The hydrogen bonding of SCN^- with hexafluropropan-2-ol and with 4-chlorophenol is similar to its association with NH_4^+ or NHR_3^+.

3- 10-P EFFECT OF CARBON TETRACHLORIDE AND AROMATIC CO-SOLVENTS ON THE METHANOLYSIS OF t-ALKYL HALIDES

C.A.N. VIANA*, M.L.S. LOPES*, B.J. HEROLD**, M.R.Q. GODINHO**

**Centro de Electroquimica e Cinética da Universidade de Lisboa,*
Faculdade de Ciencias, 1294 Lisboa Codex, PORTUGAL
***Centro de Processos Químicos da Universidade Técnica de Lisboa,*
Instituto Superior Têcnico, 1096 Lisboa Codex, PORTUGAL.

In order to explain the observed rate enhancement in the methanolysis of saturated tertiary halides caused by presence of aromatic co-solvents and carbon tetrachloride, previously reported by us [1,2] we have continued with kinetic and thermodynamic studies, as well as with the study of several properties of the binary solvent mixtures involved.

We present the kinetic and thermodynamic results of methanolysis of 2-chloro-2-methylpropane, 3-chloro-3-ethylpentane and 1-bromo-adamantane in the presence of p-xylene and of CCl_4, at different temperatures, confirming the catalytic effect of these co-solvents.

We also present surface tension results for the binary mixtures methanol + p-xylene and methanol + carbon tetrachloride, showing no self-micellisation, as well as the results of NMR and $E_T(30)$ and Y parameter studies, showing the existence of critical transition concentrations in the behaviour of these solvent mixtures.

All these studies point to a specific co-solvent-solvent interaction as principal cause for the observed effect, and show that the rate enhancement is mainly dependent on preferential solvation of the transition state, which preceeds the ion-pair, by methanol.

1. - VIIth International Conference on Non-Aqueous Solutions, Regensburg, (1980).
2. - VIth National Meeting of Chemistry, Aveiro, (1983).

3-10(P) EFFECT OF CARBON TETRACHLORIDE AND AROMATIC CO-SOLVENTS ON THE METHANOLYSIS OF t-ALKYL HALIDES
C.A.N. Viana, M.I.S. Lopes, B.J. Herold, M.R.Q. Godinho, PORTUGAL

4-5(P) APPRAISAL OF VISCOSITY B COEFFICIENTS FOR THE BROMIDE ION IN SOME NONAQUEOUS SOLVENTS OBTAINED FROM GRAPHICAL EXTRAPOLATION
K.G.Lawrence and A. Sacco, Bari, ITALY

4-6(P) TRANSFERENCE NUMBERS OF DILUTE AQUEOUS ZINC CHLORIDE SOLUTIONS BY THE INDIRECT MOVING BOUNDARY METHOD
B. Sangchakr and K. (Indaratna) Kriausakul, Bangkok, THAILAND

4-7(P) INTERMOLECULAR INTERACTIONS IN BINARY MIXTURES OF N,N-DIMETHYLMETHANESULFONAMIDE WITH ALIPHATIC ALCOHOLS. A VISCOMETRIC STUDY
L. Pikkarainen, Oulu, FINLAND

4-8(P) VISCOSITY OF Na_2SO_4 and $MgSO_4$ SOLUTIONS IN EtOH-WATER MIXTURES AT 15, 25 and 35 °C
A. Vivo, C. Quintana, M. Sanchez and C. Moran, Canary Islands, SPAIN

CHANGES TO PRELIMINARY PROGRAMME GIVEN IN THIRD CIRCULAR

2-14(O) will be read by Dr. M. Dunn
4-12(O) will be read by Dr. W.E. Waghorne
3-14(O) will be presented as poster 3-10(P)
2-9(P) will be presented as paper 2-25(O)

THE FOLLOWING CONTRIBUTIONS INCLUDED IN THE BOOK OF ABSTRACTS HAVE BEEN WITHDRAWN

Papers 1-3, 2-4, 2-8, 3-5, 5-6, 5-12

Posters 2-1, 2-12, 3-7, 3-8, 5-7, 2-5

3-18 (O) COSPHERE-COSPHERE INTERACTIONS IN KINETIC SALT EFFECTS

M.J. BLANDAMER,[a] J. BURGESS,[a] B. CLARK,[a] A.W. HAKIN [a] and J.B.F.N. ENGBERTS [b]

[a]*Department of Chemistry, University of Leicester, Leicester,*
LE1 7RH, ENGLAND

[b]*Department of Organic Chemistry, University of Groningen,*
Groningen, THE NETHERLANDS.

Kinetic data are reported for the hydrolysis of phenyl dichloroacetate and of p-methoxyphenyl dichloroacetate in aqueous salt solutions. The rate of reaction is first order in ester and depends on the composition of solvent.

Rate constants for hydrolysis are reported in aqueous salt solutions at fixed concentration of added salt; 0.9 mol dm^{-3}. Previously we reported [1] that, for the phenyl ester, the order for the bromide salts is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$ whereas the order for the fluorides is $Bu_4N^+ > Et_4N^+ > Me_4N^+ > Cs^+ > Rb^+ > K^+ > Na^+$. A similar pattern emerges for the p-methoxyphenyl ester. The dependences of log (k/k_o) (where k_o = the rate constant in aqueous solution containing no added salt) on anion shows a pattern through the cations which closely resembles the dependence of log $\gamma_\pm$ on anion where $\gamma_\pm$ is the mean ionic activity coefficient.

These patterns are examined in terms of interaction between co-spheres of solutes in solution where the organisation of solvent within the co-spheres are either compatible or incompatible.

1. J.B.F.N. Engberts, M.J. Blandamer, J. Burgess, B. Clark and A.W. Hakin, *J. Chem. Soc. Chem. Commun.*, 1985, 414-415.

4-5(P) Amended

APPRAISAL OF VISCOSITY B COEFFICIENTS FOR THE BROMIDE ION IN SOME NONAQUEOUS SOLVENTS OBTAINED FROM GRAPHICAL EXTRAPOLATION.

K.G. Lawrence and A. Sacco

Department of Chemistry, Birkbeck College, London.
Department of Chemistry, University of Bari, Italy.

Viscosity B coefficients for a series of tetra-alkylammonium bromide salts dissolved in dimethyl sulphoxide, dimethylformamide, acetonitrile and hexamethyl-phosphoric triamide have been determined at 25°C. The B coefficients have been plotted as functions of various properties of the salts studied, and the collinear points extrapolated to obtain ionic B values for the bromide ion. These values are compared with the $B(Br^-)$ values obtained using the reference salts Bu_4NBu_4B and Ph_4PPh_4B.

4-6 (P) TRANSFERENCE NUMBERS OF DILUTE AQUEOUS ZINC CHLORIDE SOLUTIONS BY THE INDIRECT MOVING BOUNDARY METHOD

B. SANGCHAKR, and K. (Indaratna) KRIAUSAKUL
Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, THAILAND.

The transference numbers of zinc ion-constitutent [1] in dilute aqueous zinc chloride solutions were determined at 25 °C. The indirect moving boundary cell and technique developed by Indaratna [2,3] were employed. The values for the zinc ion-constituent transference number for 0.003-0.09 mol kg^{-1} zinc chloride solutions were obtained with 0.15% precision. From the graphical and theoretical analyses of the data, the limiting zinc ion-constituent transference number was found to be 0.410 ± 0.002.

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1. M. Spiro, *Transference Numbers in Physical Methods of Chemistry* Part II A, 205-295, A. Weissberger Ed., Wiley & Sons, New York, (1971).

2. K. Indaratna, Ph.D. Thesis, Otago University, (1980).

3. K. Indaratna, A.J. McQuillan, and R.A. Matheson, *J.C.S. Faraday Trans I* (on submission).

0-7(P) INTERMOLECULAR INTERACTIONS IN BINARY MIXTURES OF N,N-DIMETHYLMETHANESULFONAMIDE WITH ALIPHATIC ALCOHOLS. A VISCOMETRIC STUDY

LIISA PIKKARAINEN

Department of Chemistry, University of Oulu, SF-90570 Oulu, FINLAND.

Viscosities of binary mixtures of N,N-diethylmethanesulfonamide with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, and 2-methylpropan-2-ol have been measured at 303.15 K. The excess viscosity and the excess Gibbs energy of activation of flow have been calculated from the experimental data and are represented graphically as functions of composition. Both η^E and $\Delta G^{\ddagger E}$ are negative over the entire composition ranges for all the mixtures studied, except for methanol-containing mixtures, which exhibit positive values of $\Delta G^{\ddagger E}$. The values decrease as the length of the alkyl chain of the primary alcohol increases and are smaller for the secondary and the tertiary alcohols than for the primary analogues. The results have been related to solute-solute and solute-solvent interactions in these mixtures.

4- 8 (P) VISCOSITY OF Na_2SO_4 and $MgSO_4$ SOLUTIONS IN EtOH-WATER MIXTURES AT 15, 25 and 35 °C.

A.VIVO, C.QUINTANA, M.SANCHEZ and C. MORAN
Department of General Chemistry, University of La Laguna, Canary Islands, SPAIN.

The viscosities of the associated electrolytes sodium and magnesium sulphate have been measured in the following $EtOH-H_2O$ mixtures: 0,5,10,15,20,25 and 30 % in weight of EtOH at 15, 25 and 35 °C. Previous papers, concerning 1:1 electrolytes which do not show ionic association in these $EtOH-H_2O$ mixed solvents, have shown the applicability of the Jones-Dole equation as a quantitative formulation of the Grüneisen effect and ion-solvent interaction. To obtain more information about the alcohol medium as solvent for a wide range of electrolytes, we have undertaken the study of the relative viscosities of solutions of sodium and magnesium sulphate in $EtOH-H_2O$ mixtures. Here the Jones-Dole equation, $\eta_r=1+Ac^{\frac{1}{2}}+Bc$ (with c being the concentration of the initial salt and not that of the free ions), may show a lesser concordance with the results as ionic association is occurring [1]. The plots of $(\eta_r-1)/c^{\frac{1}{2}}$ versus $c^{\frac{1}{2}}$ are perfectly linear, and the fact that the electrolytes are associated into ion-pairs, mainly the $MgSO_4$ [2],does not seem to have any initial influence.

The ion-ion interactions remain constant throughout the different mixtures, with slight increases due to temperature increase, a fact which was to be expected where the solvent structure is altered to a lesser degree, and the ionic solvation in conditions of extreme dilution must be proportional to the electronic density of the ions, i.e. higher in the Mg^{++} than in the Na^{+}. At each temperature, the B-coefficient of the sodium sulphate decreases with decrease in polarity, a decrease which is in inverse ratio to the temperature. In the magnesium sulphate, the B-coefficients are practically constant in the different mixtures at the three temperatures. In the case of the 2:1 salt, where the ionic association is 20 to 50 times less than in the $MgSO_4$, and relatively small, the temperature coefficient $(dB/dT)_{EtOH}$ is always positive. In the case of the $MgSO_4$ the behaviour is the opposite and in each solvent the $(dB/dT)_{EtOH}$ coefficient either decreases very slightly or is zero and $(dB/dX)_T$ increases slightly.

The relation of the Walden product to the B_i-coefficients is linear in all the mixtures with an opposing behaviour between the Na^{+} and Mg^{++} ions, and an intermediate one for the $SO_4^{=}$. For the cations, the viscosity coefficients decrease with the increase of the ionic radii as the percentage of ethanol increases, going through a minimum around 1.5 Å, and increasing afterwards for the anions, according to their size, as the solvent polarity decreases, i.e., $(dB_i/dr_i)EtOH$ is positive or negative depending on whether it is an anion or a cation, respectively.

1. P.B. Das, *Electrochim. Acta 22*, 1275 (1977)
   C.W. Davies and V.E. Malpass, *Trans. Faraday Soc.*, 60, 2075 (1964)
2. A. Vivo et al., *An Quim.* 77, 204 (1981)

4-16(0) TRANSFERENCE NUMBERS FOR AQUEOUS SOLUTIONS OF SODIUM DODECYLSULFATE WITH AND WITHOUT 1-HEPTANOL

Robert L. KAY and Kuo-Shin LEE
Carnegie-Mellon University, Department of Chemistry, 4400
Fifth Avenue, Pittsburgh, Pa. 15213, U.S.A.

We have measured cation transference numbers for sodium dodecylsulfate, with and without 1-heptanol, from well below to well above the critical micelle concentration, by the moving boundary method. These measurements were made possible by the radio frequency moving boundary detector. The addition of 1-heptanol causes the conductance of aqueous sodium dodecylsulfate to decrease and then increase at higher concentrations of the long-chain alcohol. The cation transference numbers, on the other hand, decrease continuously to extremely low values on addition of 1-heptanol. The results can be interpreted in terms of an inclusion of the long chain alcohol into the dodecylsulfate micelle and by the resulting dissociation of sodium ions.

4-17(O) ANALYSIS OF THE CONDUCTANCES OF SOME AQUEOUS SOLUTIONS OF CADMIUM AND ZINC BY THE LEE AND WHEATON EQUATION.

S. ADULDECHA, and K. (Indaratna) KRIAUSAKUL
Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, THAILAND.

The application of the Lee and Wheaton equation [1,2,3] to the analysis of the conductance of the associated unsymmetrical electrolyte, $CdCl_2$ in aqueous solutions [4-7] still requires further investigation. The conductance of simpler solution systems of cadmium, e.g. $Cd(ClO_4)_2$ solution, a completely dissociated unsymmetrical electrolyte, and $CdSO_4$ solution, an associated symmetrical electrolyte were therefore analysed by this equation. Multiparameter-curve-fitting optimisation was used to determine the values of the limiting equivalent conductivity of Cd^{2+}, the distance of closest approach, and the association constant. Similar investigations were also carried out for aqueous solutions of zinc salts. Careful consideration of the results suggests that there remain certain limitations in the application of the Lee and Wheaton equation to unsymmetrical salts of cadmium and zinc. The limiting equivalent conductivities of Cd^{2+} and Zn^{2+} reported here have the values of 53.1 ± 0.1 $cm^2\Omega^{-1}$ $equiv^{-1}$ and 53.5 ± 1.5 $cm^2\Omega^{-1}$ $equiv^{-1}$, respectively.

1. W.H. Lee,and R.J. Wheaton, *J.C.S. Faraday Trans. II* 74, 743-766, (1978).

2. W.H. Lee, and R.J. Wheaton, *J.C.S. Faraday Trans. II* 74, 1456-1482, (1978).

3. W.H. Lee, and R.J. Wheaton, *J.C.S. Faraday Trans. II*, 75, 1128-1145, (1979).

4. K. Indaratna, Ph.D. Thesis, Otago University, (1980).

5. K. Indaratna, A.J. McQuillan, and R.A. Matheson, *J.C.S. Faraday Trans. I* (for submission).

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7. S. Katayama, *J.Solution Chem.* 5, 241-248, (1976).

Seventh International Symposium
on
Solute-Solute-Solvent Interactions

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	MONDAY 15TH JULY AFTERNOON	
14.00 - 14.20	FORMAL OPENING OF THE 7TH INTERNATIONAL SYMPOSIUM ON SOLUTE-SOLUTE-SOLVENT INTERACTIONS	
14.20 - 15.20	Plenary Lecture - Theme 1 Prof. R. H. Wood, University of Delaware, U.S.A. Experimental and theoretical investigations of aqueous solutions at high temperatures. CHAIRMAN: DR. A. D. PETHYBRIDGE	
	ROOM 1 CHAIRMAN: DR. T. H. LILLEY	ROOM 2 CHAIRMAN: PROF. P. J. ROSSKY
15.20 - 16.00	Session Lecture - Theme 1 Prof. F. Millero, University of Miami, U.S.A. The physical chemistry of natural waters.	Session Lecture - Theme 2 Prof. K. Heinzinger, Max Planck Institute, Mainz, F.D.R. Molecular dynamic simulations of aqueous electrolyte solutions
16.00 16.30	TEA	TEA
	ROOM 1 CHAIRMAN: DR. T. H. LILLEY	ROOM 2 CHAIRMAN: PROF. P. J. ROSSKY
16.30 - 16.50	5-1 The Debye-Hückel parameters for electrolyte solutions. R.L. Kay, (Pittsburgh, U.S.A)	2-1 Molecular dynamic simulation of liquid water. G. C. Lie and E. Clementi, (New York, U.S.A.)
16.50 - 17.10	5-2 Hydration of cations and its role in their adsorption on oxides M.A. Malati, (Chatham, U.K.)	2-2 Orientational correlations in water and aqueous solutions. G. Palinkas and K. Heinzinger,(Mainz, F.D.R.)
17.10 17.30	5-3 Thermodynamic molar properties of aqueous nonelectrolyte solutions using sound velocity measurements. M.M. Emara and N.A. Farid, (Cairo, Egypt)	2-3 A molecular dynamic simulation study of an aqueous LiI solution between fixed walls. E. Spohr and K. Heinzinger,(Mainz, F.D.R.)
17.30 17.50	5-4 Temperature dependence of density, partial volume, and expansivity of liquids, liquid mixtures, and solutions. H. Craubner, (Stuttgart, F.D.R.)	

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<table>
<tr><td></td><td colspan="2">TUESDAY 16TH JULY MORNING</td></tr>
<tr><td>9.00 - 10.00</td><td colspan="2">Plenary Lecture - Theme 2 Prof. J. E. Enderby, University of Bristol, U.K.
Ionic hydration by neutron scattering
Chairman: Dr. T.M. Hardman</td></tr>
<tr><td rowspan="2">10.00 - 10.40</td><td>ROOM 1 CHAIRMAN: PROF. K. HEINZINGER</td><td>ROOM 2 CHAIRMAN: DR. M. ABRAHAM</td></tr>
<tr><td>Session Lecture - Theme 2
Prof. P.J. Rossky, University of Texas, Austin, U.S.A.
Theoretical studies of aqueous solution structure</td><td>Session Lecture - Theme 3
Prof. E.U. Franck, University of Karlsruhe,Karlsruhe, F.D.R
Aqueous mixtures in supercritical temperatures and at high pressure.</td></tr>
<tr><td>10.40 - 11.10</td><td>COFFEE</td><td>COFFEE</td></tr>
<tr><td>11.10 - 11.30</td><td>ROOM 1 CHAIRMAN: PROF. K. HEINZINGER
2-5
Dynamics of dielectric enrichment in solvent mixtures.
P. Suppan, (Fribourg, Switzerland)</td><td>ROOM 2 CHAIRMAN: DR. M. ABRAHAM
5-5
Thermodynamics of solutions from the grand partition function of the McMillan-Mayer (MM) level: relationship with the Friedman excess functions.
J.L. Gómez-Estévez, (Barcelona, Spain)</td></tr>
<tr><td>11.30 - 11.50</td><td>2-6
Dynamic hydration structure in dilute aqueous solutions of nonelectrolytes
K. Nakanishi, H. Tanaka and T. Ishibashi, (Kyoto, Japan)</td><td>5-7
Solvent effects of the electrochemical oxidation of chromium pentacarbonyl complexes $Cr(CO)_5L$
M.A. Santa Ana, I. Chadwick, C. Diaz, N, Yutronic and G. González, (Santiago, Chile).</td></tr>
<tr><td>11.50 - 12.10</td><td>2-7
Computer simulation of amino acid and nucleic acid solutions.
J.M. Goodfellow and P.L. Howell, (London, U.K.)</td><td>5-8
Solvent-solvent and solvent-solute interactions in protic and aprotic systems.
S. Wasif and S.B. Salama, (Zagazig, Egypt) amd S. ElKadry and O. Dabbit, (Aleppo, Syria).</td></tr>
<tr><td>12.10 - 12.30</td><td>2-25
Ionic association of NH_4SCN in dimethylformamide and in tetrahydrofuran
J. Rannou and M. Chabanel,(Nantes, France.)</td><td>5-9
Temperature dependence of solute-solute and solute-solvent interactions in aqueous solutions of the homologous series of n-dodecylpolyethyleneglycol surfactants, $C_{12}EO_m$(m=4,5,6 and 8)
T.M. Herrington and S.S. Sahi, (Reading, U.K.)</td></tr>
</table>

TUESDAY 16TH JULY AFTERNOON

	ROOM 1 CHAIRMAN: PROF. J.E. ENDERBY	ROOM 2 CHAIRMAN: PROF. R. L. KAY	ROOM 3 CHAIRMAN: DR. J. B. GILL
14.00 - 14.20	2-9 Water Dynamics in aqueous salt solutions; a N.M.R. contribution. J.R.C. Van der Maarel, D. Lankhorst and J.C. Leyte, (Leiden, The Netherlands)	4-1 Temperature dependence of ion association of $[Co(gly)(en)_2]^{2+}$ with sulfate and oxalate ions in water. H. Yokoyama, (Yokohama, Japan) and K. Yamamoto , (Yokohama, Japan)	3-1 A study of hydrogen-bonded species of acetic acid in water. S. Dhabanandana, P. Karntiang and V. Ruangpornvisuti,(Chulalongkorn, Thailand)
14.20 - 14.40	2-10 Proton chemical shifts of hydrogen bound to oxygen in aluminium(III) complexes with mixed water and alcohol ligands. J.W. Akitt and H. Robinson (Leeds, U.K.) and J. Lelievre, (Paris, France).	4-2 Possible dimerization of some substituted benzoic acids. L.E.Strong, R. Ryther, (Richmond, U.S.A.) and A.D. Pethybridge (Reading, U.K.)	3-2 Solute-solvent and solvent-solvent interaction parameters for infinitely dilute solutions of haloalkanes in squalane-dinonylphthalate mixtures: evidence for weak 1:1 haloalkane:dinonylphthalate complexes. G.A.Oweimreen,(Dhahran, Saudi Arabia)
14.40 - 15.00	2-11 Quadropole relaxation of ionic nuclei as a probe for local symmetry and selective solvation in electrolyte solutions. M. Holz, (Karlsruge, F. D.R.) and A. Sacco (Bari, Italy).	4-3 Properties of selected non-aqueous $LiClO_4$ solutions from conductance measurements and Fuoss equation analyses. L. Werblan, A. Suzdorf, J. Lesiński and G. Szymański, (Warsaw, Poland).	3-3 On the acidity function H_0 and solvent composition H. Sadek, (Alexandria, Egypt)
15.00 - 15.20	2-12 Sodium cation complexation by large crown ethers in low donicity solvents. C. Detellier and H.D.H. Stover, (Ottawa, Canada) and A. Delville, (Liege, Belgium)	4-4 The first ionization constant of ortho-phosphoric acid to 250 °C and to 2000 bar. A.J. Read, (Petone, New Zealand).	3-4 Spectroscopic and conductance evidence for solute-solute interactions in phenol and butenone derivatives. O. Dabbit, S.El Kadry and S. Wasif (Aleppo, Syria)
15.20 - 15.40	2-13 Solvation equilibria and intramolecular dynamics in mixed complexes of neutral bidentate organophosphorus ligands as studied by N.M.R. T. Chniber, L.Rodehüser, P.R.Rubini and J.J.Delpuech, (Vandoeuvre, France)	4-5 Solvent isotope effect on mobility of K^+ and Cl^- ions in compressed water. M. Nakahàra, (Kyoto, Japan)	3-6 Thermodynamics of transfer of tris-(hydroxy methyl)-aminomethane and p-nitroaniline indicator from water to aqueous-2-methoxyethanol mixtures. Solvent effect on the dissociation of their protonated bases. A.A.El-Harakany and A.O.Barakat,(Alexandria, Egypt)
15.40 - 16.00	2-14 Studies of the interaction of cobalt complexes with hydrogen bonding solvents using ^{59}Co NMR. D.R. Eaton, (Ontario, Canada)	4-6 Conductance behaviour of some silver(I) salts in water-acetonitrile and methanol-acetonitrile mixtures. C. Kalidas and S. Subramanian,(Madras, India)	3-18 Cosphere-cosphere interactions in kinetic salt effects. M.J.Blandamer, J.Burgess, B.Clark, A.W.Hakin (Leicester, U.K.), J.B.F.N. Engberts (Gronigen, The Netherlands)
16.00 - 15.30	TEA	TEA	TEA
15.30 - 17.50	POSTER SESSION 1, ROOM 4		

	WEDNESDAY 17TH JULY MORNING	
9.00 - 10.00	R.A. Robinson Memorial Lecture Dr. K.H. Khoo University of Malaysia, Kuala Lumpur, Malaysia Activity Coefficients in Mixed Electrolyte Solutions Chairman: Prof. H.M. Frey (University of Reading, on behalf of the Royal Society of Chemistry)	
	ROOM 1 CHAIRMAN: PROF. R.L. KAY	ROOM 2 CHAIRMAN; DR. L.A. WOOLF
10.00 - 10.40	Session Lecture - Theme 4 Prof. J. Barthel, University of Regensburg, F.R.G. Data on transport properties of electrolyte solutions for applied research and technology.	Session Lecture - Theme 3 Dr. M. Abraham, University of Surrey, U.K. Solvent effects on reaction rates.
10.40 - 11.10	COFFEE	COFFEE
	ROOM 1 CHAIRMAN: DR. J.C. JUSTICE	Room 2 CHAIRMAN: DR L.A. WOOLF
11.10 - 11.30	2-15 Structure of thiocyanato complexes of zinc(II), cadmium(II) and mercury(II) in aqueous solution. H. Ohtaki, K.Yamamoto and T.Yamaguchi, (Yokohama, Japan)	5-10 Solute-Solute interactions of organic model compounds in nonaqueous solvents: relevance for the native conformation of proteins M.Bloemendal and G.Somsen, (Amsterdam, The Netherlands)
11.30 - 11.50	2-16 The structure of tin(II) aqua and halide complexes in aqueous solution by means of EXAFS and X-ray diffraction. T. Yamaguchi,(Yokohama, Japan), O. Lindqvist, (Gothenburg, Sweden), T. Claeson, (Gothenburg, Sweden) and J.B. Boyce, (California, U.S.A.)	5-11 Preferential solvation and hydrophobic hydration of saccharides in mixtures of N,N-dimethylformamide and water. R.W. Balk and G. Somsen, (Amsterdam, The Netherlands)
11.50 - 12.10	2-17 The solvated gold(I) ion in pyridine solution: a tetrahedral complex of gold(I) S. Ahrland, K. Nilsson, A. Oskarsson, I. Persson and A. Yuchi, (Lund, Sweden)	4-16 Transference numbers for aqueous solutions of sodium dodecylsulphate with and without 1-heptanol. R.L. Kay and K.S. Lee, (Pittsburgh, U.S.A.)
12.10 - 12.30	2-18 On the solvation of methylmercury(II) compounds. I. Persson, (Lund, Sweden) and Å. Iverfeldt (Göteborg, Sweden)	4-17 Analysis of the conductances of some aqueous solutions of cadmium and zinc salts by the Lee-Wheaton equation. S. Aduldecha and K. Kriausakul,(Bangkok, Thailand)

THURSDAY 18TH JULY MORNING

9.00 - 10.00	Plenary Lecture - Theme 3 — Prof. P. Laszlo, University of Liege, Belgium Local order due to electrostatic interactions Chairman: Dr. A.K. Covington	
	ROOM 1 CHAIRMAN: DR. M. SPIRO	***ROOM 2 CHAIRMAN: PROF. F. MILLERO***
10.00 - 10.40	Session Lecture - Theme 4 Dr. L.A. Woolf, Canberra, Australia. Insights into solute-solute-solvent interactions from transport property measurements with particular reference to methanol-water mixtures and their constituents.	Session Lecture - Theme 1 Dr. M. Whitfield, M.B.A., Plymouth, U.K. Chemical speciation in natural waters - a cautionary tale.
10.40 - 11.10	COFFEE	COFFEE
	ROOM 1 CHAIRMAN: PROF. J. BARTHEL	**ROOM 2 CHAIRMAN: PROF. F. MILLERO**
11.10 - 11.30	4-7 Transference numbers in concentrated alkali chloride solutions M. Spiro, D. Panopoulos and H. Kaneko, (London, U.K.)	1-1 Electrolyte solutions near the critical point of water. D.J. Turner, (Leatherhead, U.K.)
11.30 - 11.50	4-8 Aqueous solutions of zinc halides: an exceptional class of electrolytes H. Weingärtner and K.J. Müller, (Karlsruhe, West Germany)	1-2 Specific heat capacities of pure water and seawater at high pressures. C.T.A. Chen (Oregon, U.S.A.)
11.50 - 12.10	4-9 Ionic self-diffusion in the methanol-water-NaCl system. E. Hawlicka and W. Reimschüssel, (Lódź, Poland)	1-4 The prediction of scale formation in oilfield brines G. Atkinson and B.L. Atkinson, (Norman, U.S.A.)
12.10 - 12.30	4-10 Polyaromatic compounds as high temperature solvents for ionic salts. G. Geblewicz, R. Potter and D. Schiffrin, (Southampton, U.K.)	

	THURSDAY 18TH JULY AFTERNOON.	
	ROOM 1 CHAIRMAN: DR. M. WHITFIELD	ROOM 2 CHAIRMAN: PROF. P. LASZLO
14.00 - 14.20	2-19 A study of the structure of water and aqueous solutions, based on the isotope effects on solvation thermodynamics. Y. Marcus and A. Ben-Naim, (Jerusalem, Israel)	3-7 First determinations of stability constants in liquid ammonia solutions using potentiometric titrations: cyano- and thiocyano-silver(I) complexes at 233 K Y.M. Cheek, P. Gans and J. Bernard Gill, (Leeds, U.K.)
14.20 - 14.40	2-20 Interaction between alcoholic OH groups and non-polar solvents; a spectroscopic study. W.A.P. Luck, T. Mentel and S. Peil, (Marburg, West Germany)	3-8 Solution and protonation of purines and related bases in dimethylsulfoxide. R.L. Benoit and M. Fréchette, (Québec, Canada)
14.40 - 15.00	2-21 Interactions of cations with "soft" donor solvents. G. Gritzner, (Linz, Austria)	3-9 Thermodynamics in non-aqueous solvents, uranyl(VI) complexes with amines in dimethyl sulfoxide. A.Cassol, P. Di Bernardo, G. Tomat and P. Zanonato, (Padova, Italy) and R. Portanova and M. Tolazzi, (Udine, Italy)
15.00 - 15.20	2-22 Metal complexes as colour indicators for solvent parameters. R.W. Soukup and R. Schmid, (Vienna, Austria)	3-10 Solvation and slow solvent exchange processes on six-coordinate lanthanides. A kinetic and mechanistic study. S.F. Lincoln and A. White, (Adelaide, Australia)
15.20 - 15.40	2-23 Raman spectral studies of iron(III) chloride solutions. K. Murata, D.E. Irish and G.E. Toogood, (Ontario, Canada)	3-11 Complex formation of bivalent metal ion with moncamino-monocarboxylic acids. H. Matsui, (Nagoya, Japan)
15.40 - 16.00	2-24 Preferential solvation studies of sodium iodide in ethyleneglycol [EG] + acetonitrile [AN] and in propylene glycol [PG] + acetonitrile [AN] mixtures. A.K. Covington and M. Dunn, (Newcastle-upon-Tyne, U.K.)	3-12 Effect of solvent polarity and of substituents on equilibria in the systems: Me(II) - TMU solvent. J. Maslowska and K. Wojtysiak, (Lódź, Poland)
16.00 - 16.30	TEA	TEA
16.30 - 17.50	POSTER SESSION 2, ROOM 4	

	FRIDAY 19TH JULY MORNING	
9.00 - 10.00	Plenary Lecture - Theme 4 Dr. J. C. Justice, University of Pierre and Marie Curie, Paris, France Theories of transport properties using the Onsager treatment. Chairman: Prof. J. Barthel	
	ROOM 1 CHAIRMAN: DR. M. SPIRO	ROOM 2 CHAIRMAN: DR. A.K. COVINGTON
10.00 - 10.20	4-11 Phenomenological relationship between the fluidity and mobility in concentrated electrolyte solutions. K. Tanaka and R. Tamamushi, (Saitama, Japan)	3-13 Reaction of ethyl iodide with bromide ion. Reaction rates and transfer enthalpies of anions in N-methylacetamide + acetonitrile and N-methylacetamide + N,N,-dimethylacetamide mixtures. Y.Kondo, A.Nakano and S.Kusabayashi, (Osaka, Japan)
10.20 - 10.40	4-12 A new theory of the viscosities of electrolyte solutions D. Feakins and K.G. Lawrence, (London, U.K.) add W.E. Waghorne (Dublin, Eire)	3-15 Evidence for a complex mechanism of t-butyl halide solvolysis. R.M.C. Goncalves, F.E.L. Martins and A.M.N. Simoes, (Lisboa, Portugal)
10.40 - 11.10	COFFEE	COFFEE
11.10 - 11.30	4.13 Contributions of long-range solvent perturbations to viscosities and volumes of electrolyte solutions. W. Seidel, (Giessen, West Germany)	3-16 The nuetral hydrolysis of two 1-acryl-1,2,4-triazoles in binary aqueous mixtures: isobaric versus isochoric activation parameters. J.R.Haak and J.B.F.N. Engerts, (Groningen, The Netherlands) and M.J. Blandamer, (Leicester, U.K.)
11.30 - 11.50	4-14 Comparison of viscosity and enthalpy of dissolution of 1:1 and 2:1 electrolytes in water-organic solvent mixtures. S. Taniewska-Osinska, A. Kacperska, J. Barczynska, N.Jóźwiak and B. Nowicka, (Lódź, Poland)	3-17 The solubilization of organic solutes by aqueous micellar solutions. S.D. Christian and E.E.Tucker, (Norman, U.S.A.) and J.F. Scamehorn, (Norman, U.S.A.
11.50 - 12.10	4-15 Studies on solute-solvent interactions from viscosity measurements with particular reference to high concentration range of alkali halides in aqueous lactose solution. A.K. Singh, P.N. Tripathi and V.K.Singh, (Varanasi, India)	
12.10 12.30	Closing talk Prof. R.H. Wood, University of Delaware, U.S.A. Chairman. Dr. A.D. Pethybridge	