Evidence of Complex Formation in Concentrated Solutions by X-Ray Diffraction Technique

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For several years remarkable contributions to the knowledge of the coordination of metal ions in solutions have been provided by X-ray diffraction studies. The description of the structure of the solutions is usually confined to the first coordination shell of the ions in terms of distances, geometries and coordination numbers. Recently, attempts have been made to describe interactions arising from the second coordination shell of the cations [1]. Further complex formation has been found to be successfully examined by this technique. The structure of complexes in solution, in fact, can often be obtained in a unique way if the scattering measurements are carried out for solutions of different concentration and/or composition and the results are combined with equilibrium analysis and crystal structure determination.

X-ray analysis can be performed in several ways. When dealing with solutions of heavy atoms information on the dominant intramolecular interactions can be easily obtained from the high-angle part of a scattering curve by means of a least square procedure which yields the bond lengths and the frequency of the distances, while the low-angle part can be used to obtain information on the packing of solvent molecules around the complex. With light atom solutions the scattered intensities from the cations are levelled of to the other contribution in solution: a complete model is needed to perform a least square procedure, and for its formulation, the greatest amount of information must be drawn from the experimental radial curves. The use of difference curves between radial distribution functions of solutions of different concentration and/or composition is often revealing as far as the structuring of complexes in different chemical conditions is concerned.

Transition metal ions, such as Fe(III), Cr(III), Th(IV), have been investigated at different concentration in acidic, neutral and hydrolysed solutions in different chemical conditions [1]. As an exemplification of the method mononuclear complex formation between Fe(III) and typical inorganic anions (sulphate [2] and chloride [3]) will be examined. Polynuclear complex formation will be illustrated by Th(IV) hydrolysed solutions where structural units containing from few up to several tenths of atoms have been found to occur in these solutions [4].

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Rotational Correlation Times and Self-Diffusion Coefficients in Methanol–Ethanol System

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It is well known that rotational motion is strongly correlated with translational motion in polar liquids [1] and aqueous solutions of non-electrolytes [2]. The investigation on the correlation of these motions is one of the usefull approach for elucidating the structure in the mixture of polar liquids. In this report we investigate the concentration dependence of the deuteron relaxation rate $1/T_1$ of the partially deuterated alcohols CD_3OH, CD_3CH_2OH, and CH_3CD_2OH and the self-diffusion coefficients in methanol–ethanol system at 25 °C.

The measurements of the spin-lattice relaxation times and the self-diffusion coefficients have been performed with a spin-echo spectrometer JNM-FSE 60A and a S/N Booster JNM-3B-SB(JEOL). The resonance frequencies for ^1H and ^2H are 60 and 9.2 MHz, respectively. All samples were degassed and sealed.

In Fig. 1 is shown the concentration dependence of the self-diffusion coefficients of methanol and ethanol in the methanol–ethanol mixture. A minimum of self-diffusion coefficient of methanol appears at higher concentration than that of ethanol. The concentration dependence of the deutron relaxation rate $1/T_1$ of CD_3OH in C_2H_5OH is shown in Fig. 2. The deuterion relaxation rate shows a maximum at 11 mol% of methanol. In the case of methanol, there-

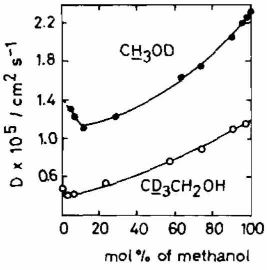

Fig. 1

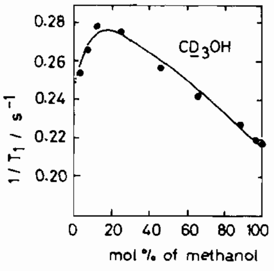

Fig. 2

fore, the self-diffusion coefficient correlates with relaxation rate. In the case of ethanol, however, both the relaxation rates of $-CD_3$ and $-CD_2$ did not show the maximum but decreased with increasing the concentration of methanol.

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Dynamical Properties of Pyrrole Dissolved in C_2Cl_4 and CH_3CN

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The aim of this paper is to examine the influence of the 'inert' solvent as C_2Cl_4 and 'active' solvent as CH_3CN on the relaxation time of pyrrole.

On the basis of the line-shape analysis imido protons (scalar relaxation of the second kind) relaxation and correlation times of pyrrole in the mentioned solvents have been calculated.

The dependence of the line-shape on solute concentration and temperature was studied and the activation parameters for molecular reorientation of pyrrole determined.

Influence of the Solvent on the Polarity of Hydrogen Bonded Complexes

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The dipole moments of complexes between carboxylic acids and triethylamine were determined in both binary mixtures and in cyclohexane and benzene solution. If a carboxylic acid is dissolved in pure triethylamine, it forms mainly a 1/1 complex of dipole moment μ_{ab}. This dipole moment and that of the pure base μ_B can be computed in the following way; one determines the experimental quantity Ω_B from the dielectric constant ϵ, the refractive index and the molar volume $\bar{V}$ of the solutions:

$$\Omega_B \equiv \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} \frac{\bar{V}}{x_B} \frac{9 \cdot 10^{36} kT}{4\pi N}$$

x_B being the mole fraction of the base.

If the dipole moments remain unchanged this quantity must vary linearly with the ratio x_A/x_B accordingly to the equation

$$\Omega_B = \mu_B^2 + (\mu_{ab}^2 - \mu_B^2) \frac{x_A}{x_B}$$

Actually the relation is not perfectly linear but shows a slight upward curvature. This can be interpreted as resulting from the influence of the increasing of the *dielectric constant* of the medium *on the dipole moment μ_{ab} of the complex.*

For acetic, propanoic, butanoic and pentanoic acid, the pK_a's of which are very similar, the points of the function $\Omega_B = f(x_A/x_B)$ lie on the same curve, indicating that the dipole moment μ_{ab} of the 1/1 complex at a given value of the dielectric constant is nearly the same for the four acids.

As a first approximation μ_{ab}^2 appears to be a linear function of the reverse of the dielectric constant. The derivative $d\mu_{ab}^2/d\epsilon^{-1}$ is of the order of 13 D^2. The same quantitative relation holds for the complexes dissolved in cyclohexane.

In benzene the derivative is smaller but the moment is markedly higher. This is explained as resulting from specific interactions between the solvent and the ab complex. Presumably these interactions involve the π electrons of benzene and the lone pair of electrons of the C=O group of the complex.

Specific Interactions of Pyridinium Ions and Pyridine Molecules in Nitrobenzene. Substituent Effects

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From conductance measurements of a series of pyridinium picrates in nitrobenzene solutions, the equilibrium constants of the following hydrogen bonding reactions were estimated for each system:

(*1*) the molecular acid–base association constant K_f,

$$\text{HPic} + \text{Py} \underset{}{\overset{K_f}{\rightleftharpoons}} \text{PyHpic}, \; K_f = \frac{[\text{PyHPic}]}{[\text{HPic}]\,[\text{Py}]}$$

(*2*) the ionic association constant K_a,