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

M. MAGINI* and G. SCIBONA

CNEN-CSN-Casaccia, Lab. Chimica Fisica, Divisione Materiali, DIP/RIT, Rome, Italy

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].

References

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

H. UEDAIRA

Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan

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-

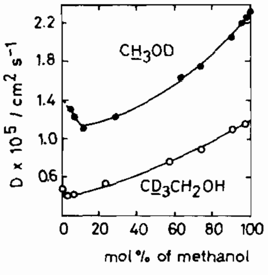

Fig. 1

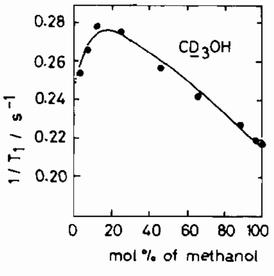

Fig. 2