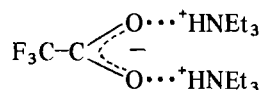


deviations occur in that the Fuoss relationship shows downward curvature. This is interpreted as due to formation of triple ions of the type $(\text{Et}_3\text{NH}, \text{CF}_3\text{COO}, \text{Et}_3\text{NH})^+$. In this range of concentrations such triple ions do not appear to a great extent in nitrobenzene when the bond between the ion and the ion pair is purely electrostatic. However in the present case, the triple ion can be stabilized by hydrogen bonds:



The constant for the formation of the triple ions has been evaluated using the method of Wooster [3].

Upon addition of an excess of CF_3COOH to the salt solutions a large decrease of the association constant K_A , and of the mobility Λ_0 is observed. This is interpreted as due to the formation of the homoconjugate anion $(\text{CF}_3\text{COOHOCFCF}_3)^-$. This 1:1 symmetric complex is characterized by a formation constant of $10^5 \text{ dm}^3 \text{ mol}^{-1}$ which is three orders of magnitude greater than the formation constant of most homoconjugate cations in nitrobenzene. The study has been extended to other substituted acetic acids in order to determine the influence of the acidity on the formation of these different types of hydrogen bonds.

References

- 1 R. M. Fuoss, *J. Am. Chem. Soc.*, 57, 488 (1935).
- 2 M. Cl. Haulait and P. L. Huyskens, *J. Solution Chem.*, 4, 853 (1975).
- 3 C. B. Wooster, *J. Am. Chem. Soc.*, 59, 377 (1937).

Structural Order in Divalent Metal Halide Aqueous Solutions

R. CAMINITI, G. LICHERI, G. PASCHINA, G. PICCALUGA and G. PINNA

Istituto Chimico Policattedra, Via Ospedale 72, 09100 Cagliari, Italy

The knowledge of local order in aqueous solutions of electrolytes and the way it changes with temperature and concentration is an important chapter of Chemical Physics of Solutions, some aspects of which are still open and strongly debated.

Recently, increasing attention has been devoted to the structure of concentrated aqueous solutions of divalent metal halides, for which qualitative changes in local ordering at increasing concentration are thought to take place.

These changes might affect:

a) the details of the structuring occurring around the cations, concerning in particular the possible formation of complexes with the halide ion nearest neighbour to the cation;

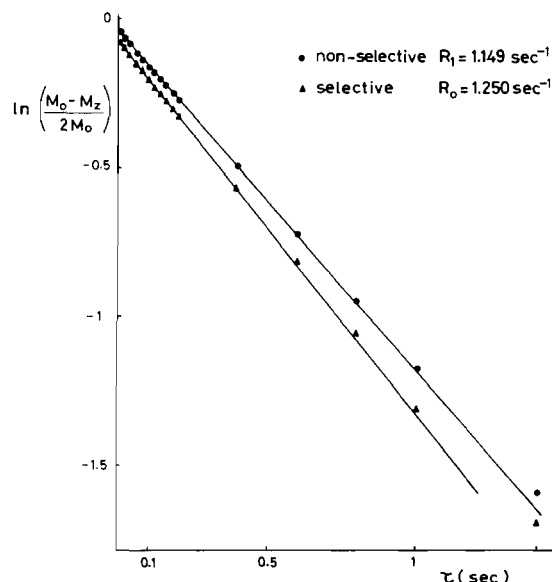
b) the possibility that, with increasing concentration a middle or long range order structure appears, which involves strong cation–cation correlation.

These two aspects are obviously connected, as the appearance of long range order phenomena should also affect the shorter distance structure around the ions.

Results obtained through different experimental techniques seem to give a non unique answer to these structural problems.

Since diffraction patterns contain the most direct information about mean molecular configurations in solution, meaningful contributions in clarifying these problems may come from X-ray diffraction studies of different electrolyte solutions at various concentrations.

Here, X-ray diffraction data analysis of concentrated aqueous solutions of CdCl_2 , NiCl_2 , and CaCl_2 are presented, as contribution to the discussions about the problems mentioned above.



Investigations of the Polyborate Equilibria in Aqueous Solutions by ^{11}B -NMR and Raman Spectroscopy

G. HELLER*, R. JANDA and J. MATHIEU

Institute of Inorganic and Analytic Chemistry, Free University Berlin, Fabeckstrasse 34/36, D-1000 Berlin 33, F.R.G.

The aim of this work was to extend our knowledge of the ions which are involved in equilibria in concen-