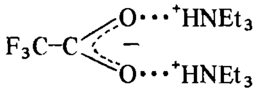
deviations occur in that the Fuoss relationship shows downward curvature. This is interpreted as due to formation of triple ions of the type $(Et_3NH, CF_3COO, Et_3NH)^+$. In this range of concentrations such triple ions do not appear to a great extent in nitrobenzene when the bond between the ion and the ion pair is purely electrostatic. However in the present case, the triple ion can be stabilized by hydrogen bonds:



$$F_3C{-}C\begin{array}{l} \diagup O\cdots{}^{+}HNEt_3 \\ - \\ \diagdown O\cdots{}^{+}HNEt_3 \end{array}$$

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 $(CF_3COOHOOCCF_3)^-$. This 1:1 symmetric complex is characterized by a formation constant of 10^5 dm^3 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.

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Structural Order in Divalent Metal Halide Aqueous Solutions

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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;

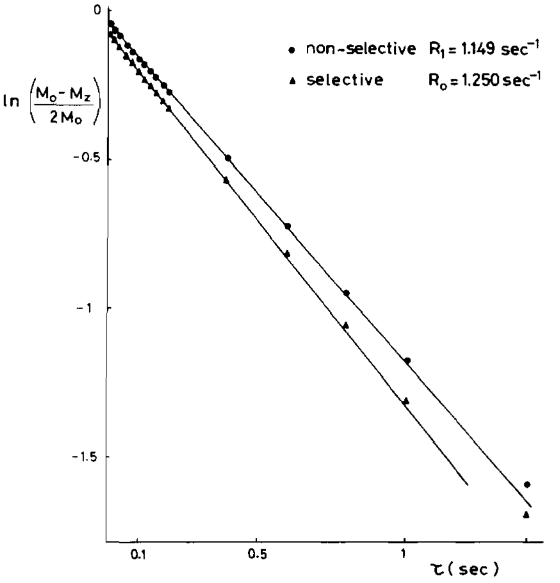
b) the possibility that, with increasing concentration a middle or long range order structure appears, which involves strong cation–cation correlation.

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

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The aim of this work was to extend our knowledge of the ions which are involved in equilibria in concentrated aqueous solutions of borates [1, 2]. The ^{11}B nuclear magnetic resonance spectra of sodium, potassium and ammonium polyborates in D_2O solutions, – as a function of concentration and pH value –, provide information of the hydrolysis equilibria. Two NMR signals are observed in the aqueous solutions of the pentaborates $Na[B_5O_6(OH)_4]$, $K[B_5O_6(OH)_4]$ and $NH_4[B_5O_6(OH)_4]$, while only one NMR line is recorded in the solutions of the tetraborates $Na_2[B_4O_5(OH)_4]$ and $(NH_4)_2[B_4O_5(OH)_4]$. A solution of $(NH_4)_2[B_4O_5(OH)_4]$ at pH 7 shows two lines again [3].

The next step was to study the Raman spectra of solid H_3BO_3, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$, $K[B_5O_6(OH)_4]\cdot 2H_2O$ and of $Na[B(OH)_4]$ as well as of borax in aqueous solutions as a function of concentration and pH, recorded between 300 and 1500 cm^{-1}.

For comparisons the Raman spectra of solid $(NH_4)_2[B_4O_5(OH)_4]\cdot 2H_2O$, β-$NH_4[B_5O_6(OH)_4]\cdot 2H_2O$, $NH_4[B_5O_6(OH)_4]\cdot 0.67H_2O$ and $NH_4[B_5O_6(OH)_4]$ were considered. In solution, all lines in the Raman spectra could be assigned and the degree of depolarization measured. The assigned Raman frequencies can be used for the identification of unknown B–O lines and therefore of unknown borate structures [4].

In the last step the influence of some series of foreign electrolytes in various concentrations of the equilibria of the borate species in a 0.5 *M* solution was investigated by Raman spectroscopy.

On the one hand, addition of the foreign electrolyte solutions has a dilution effect, so that in many of these systems there exists only the $[B(OH)_4]^-/B(OH)_3$ equilibrium without polyborates. On the other hand, the effect is sometimes a forcing of the equilibrium in favour of the polyborate formation with the triborate ions $[B_3O_3(OH)_4]^-$ and $[B_3O_3(OH)_5]^{2-}$ as predominant species. The tetraborate ion $[B_4O_4(OH)_5]^{2-}$ is present only to a minute extent, while the formation of the pentaborate ion $[B_5O_6(OH)_4]^-$ is repressed the most [5].

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A Chemical Interpretation of the Intense Raman Spectra Observed at a Silver Electrode in the Presence of Chloride Ion and Pyridine: Formation of Radicals

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During the past five years, a large number of researchers have been interested in the Raman spectroscopic study of the phenomena involved at a silver electrode immersed in an aqueous chloride solution containing pyridine. We feel that the numerous interpretations proposed (1 to 9 and references therein) to explain the 'giant' intensity enhancement of the Raman spectra observed at the silver electrode solution interface are not convincing.

The aim of this work is to show that the observed phenomenon may be explained by a simple resonance Raman effect due to radical species formed at the silver electrode–solution interface during the oxidation–reduction cycle. In the case of KCl, pyridine solution, the bands observed in Raman and electroreflectance spectroscopy at 227 cm^{-1} and 750 nm ($\Delta R/R$) are assigned to the presence of Cl_2^- radical anions. The band at 1025 cm^{-1} and the bands at 1008 and 1036 cm^{-1} as well as the shoulder at 650 nm ($\Delta R/R$) are attributed respectively to the formation of pyridinium radical cations and pyridinyl radical anions.

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Ligand Effects on Jahn–Teller Distortions. Consistent Force Field Calculations of Cu(II) Complexes

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The structural and electronic properties of Cu(II) complexes with symmetric tridentate facially coordinating ligands have recently been studied with respect to their Jahn–Teller distortions [1]. In such systems the forces opposing the Jahn–Teller distortion are of