$$PyH^+ + Pic^- \overset{K_a}{\rightleftharpoons} PyHPic, K_a = \frac{[PyHPic]}{[PyH^+][Pic^-]f_\pm^2}$$

(*3*) the homoconjugation constant K_i^+

$$PyH^+ + Py \overset{K_i^+}{\rightleftharpoons} (PyHPy)^+, K_i^+ = \frac{[PyHPy^+]}{[PyH^+][Py]}$$

In addition to these, the formation of 1:2 complexes between the pyridinium ion and the pyridine molecule is observed in the case of 3,4-dimethylpyridine and 4-dimethylamino pyridine. This may be explained in terms of π–π interactions between the second pyridine molecule and that already bound to the cation by a hydrogen bond.

Plots of $\log K_f$, $\log K_a$ and $\log K_i^+$ *vs.* aqueous pK_a s values of the pyridines yield straight lines with slope of 1.167, −0.218 and 0.061 respectively. The results show that the hydrogen bond formation between pyridine and picric acid in nitrobenzene increases with increasing basicity of the pyridine molecule. The value of the first slope indicates that the proton transfer is important. The ionic association between the pyridinium cation and the picrate anion increases with increasing acidity of the cation. In the case of the formation of the homoconjugate cation $PyH^+\cdots Py$ it was expected that the substituent effects will be small, because the increasing proton donor ability of the cation will be compensated by the decreasing proton acceptor ability of the conjugate base. It is interesting to note that, contrary to this expectation, the stability of the non-*ortho* substituted homoconjugate cation increases, although to a small extent, with the basicity of the pyridine. This is explained by considering the potential energy curve of the proton for the homoconjugate cation. The increase of the depth of the potential well resulting from the hydrogen bond formation is more important when the pyridine is more basic.

A Study of the Solvent Effect on the Raman Parameters of Halogen and Interhalogen Vibration Bands

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The ν_{Br-Br} Raman band of bromine dissolved in several solvents was studied. The observed frequency shifts relative to the gas phase value were correlated with the Krikwood–Bauer–Magat function:

$$\frac{\Delta\nu}{\nu} = C\frac{\epsilon - 1}{2\epsilon + 1}$$

Important deviations were observed for the solvents which are known to form specific charge transfer complexes with bromine, and also for CS_2.

The absolute intensity of the bromine Raman vibration band was calculated from relative intensity measurements. Also the depolarization degree ρ was measured. These measurements allowed to calculate the polarizability derivatives $(\alpha_R')_\parallel$ and $(\alpha_R')_\perp$.

The ρ factor increases when the polarity of the solvent increases or when specific interactions bromine–solvent occur. Two different relations for the inert solvents and for the interacting solvents were observed on comparing ρ with $\Delta\nu/\nu$. This must be explained by the increase of the parallel polarizability component $(\alpha_R')_\parallel$ as a result of the specific interaction with the solvent.

The half band width of the bromine band was found to be smaller than the corresponding infrared band and this is explained by the fact that the Raman band is only partially polarized. The relation between the increase of the half band width and the ρ value supports this explanation.

The results for the ν_{Br-Br} band are compared with those of a new study on the ν_{I-Br} band parameters in these solvents.

Specific Interactions of Trifluoroacetate Ion and Trifluoroacetic Acid in Nitrobenzene

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The conductances of solutions of triethylammonium trifluoroacetate ($Et_3NHCOOCF_3$) in nitrobenzene have been measured in order to study the ionic association:

$$Et_3NH^+ + CF_3COO^- \overset{K_A}{\rightleftharpoons} Et_3NH^+\cdots{}^-OOCCF_3$$

Using the Fuoss linear relationship [1] for solutions covering the concentration range 10^{-4}–10^{-3} *M*, the association constant K_A has been evaluated (K_A = $3\cdot10^5$ dm^3 mol^{-1}). This constant is two orders of magnitude greater than that observed for triethylammonium picrate in the same solvent [2] (HPic and CF_3COOH have the same aqueous pK_a's values). For salt concentrations ranging from 10^{-3} to 5.10^{-3} *M*

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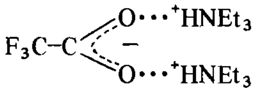
deviations occur in that the Fuoss relationship shows downward curvature. This is interpreted as due to formation of triple ions of the type (Et_3NH, CF_3COO, $Et_3NH)^+$. In this range of concentrations such triple ions do not appear to a great extent in nitrobenzene when the bond between the ion and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



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;

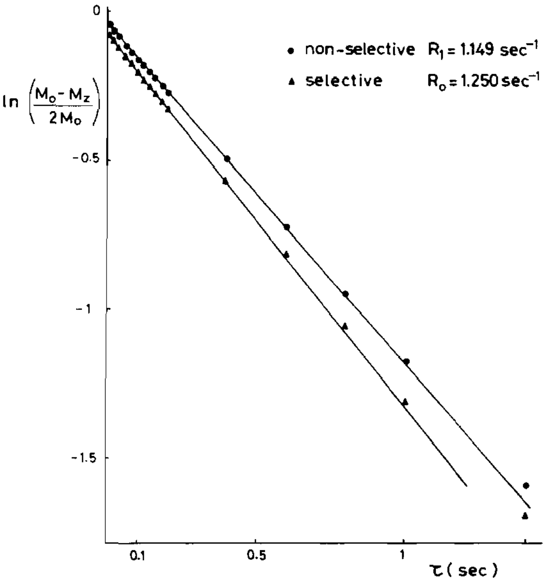
b) the possibility that, with increasing concentration a middle or long range order structure appears, which involves strong cation–cation correlation.

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 concen-