

# CHAPTER X

## CONCLUDING REMARKS

The major part of our research was concerned with the investigation of the solvation phenomena of  $\text{LiBF}_4$ ,  $\text{NaBF}_4$ ,  $\text{KPic}$ ,  $\text{KBPh}_4$ ,  $\text{Ph}_4\text{PCl}$ ,  $\text{Ph}_4\text{PBr}$ ,  $\text{Ph}_4\text{AsCl}$ ,  $\text{Ph}_4\text{AsPic}$  and  $\text{Bu}_4\text{NBPh}_4$  salts in ME, and  $\text{NaBF}_4$ ,  $\text{NaBPh}_4$  and  $\text{NaClO}_4$  in DME. This was achieved by measuring the conductance, density and ultrasonic velocity of the solutions of these electrolytes in the respective solvents, at different temperatures, and through FT-Raman spectral analysis. The viscosity of the sodium salts in DME was also determined. Excess properties of NMA + ME, NMA + water, DMA + ME and DMA + water systems were also studied, at three different temperatures. The measurements were analysed with the appropriate equations and interpreted. The findings are summarized as follows.

In ME, strong association and ion pair formation was found for all these electrolytes. The solvation weakened as soon as the ion pair was formed. Small ions like  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{Br}^-$ , and large  $\text{Pic}^-$  ions are largely solvated through electrostriction of solvent molecules around these ions. The large  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{As}^+$  ions accommodate the solvent molecules inside the space between the alkyl/aryl chain attached to the nitrogen/arsenic atom. In other words, solvent molecules penetrate into these alkyl/aryl chains. For  $\text{BPh}_4^-$  ions, neither electrostriction nor penetration of solvent molecules seems to be important.  $\text{BF}_4^-$  ions remain largely unsolvated. Conductance studies reveal that Coulombic forces play a major role in the association process. FT-Raman spectral investigations show that  $\text{LiBF}_4$ ,  $\text{NaBF}_4$ ,  $\text{Ph}_4\text{PCl}$ ,  $\text{Ph}_4\text{PBr}$  and  $\text{Ph}_4\text{AsCl}$  in ME exist as

solvent separated ion pairs and/or solvent separated dimers. They also exhibit a very intense peak for "spectroscopically free" anion.

Chelation of ME with cations takes place through the lone pair of electrons on the ethereal oxygen atom in ME. Compressibility studies, especially the sign and magnitude of the limiting apparent molar isentropic compressibility at different temperatures, are very helpful in confirming and explaining the ion pair formation. For example, the initial increase in the compressibility of  $\text{Na}^+$  and  $\text{Li}^+$  ions is due to the loss of some solvent molecules from the first coordination sphere on raising the temperature (from 288.15 to 298.15 K, in this case). However, at higher temperatures (above 298.15 K), the intramolecular hydrogen bonds begin to break down decreasing the compressibility.

In DME, conductance studies of  $\text{NaBF}_4$ ,  $\text{NaBPh}_4$  and  $\text{NaClO}_4$  in DME indicate that  $\text{NaBF}_4$  forms contact ion pairs and  $\text{NaClO}_4$  forms solvent separated ion pairs while  $\text{NaBPh}_4$  remains least solvated. These findings are supported by FT-Raman spectral studies. Viscosity measurements of  $\text{NaBF}_4$ ,  $\text{NaBPh}_4$  and  $\text{NaClO}_4$  in DME show that  $\text{ClO}_4^-$  is present as a bigger entity than  $\text{BF}_4^-$ . From the compressibility data we find that  $\text{NaClO}_4$  is more compressible than  $\text{NaBF}_4$ . This is due to the higher surface charge density of a  $\text{BF}_4^-$  ion than that of a  $\text{ClO}_4^-$  ion.

Analysis of the excess properties of the four systems indicates strong association through multiple hydrogen bonding, probably through the polar groups of the amide and

water, in the case of NMA + water and DMA + water mixtures. However, there is weak interaction and solvent structure effect in NMA + ME and DMA + ME mixtures. While the two amides behave in a similar fashion in their interaction with water, they differ much in their encounter with ME. NMA may undergo a structure-breaking effect in its interaction with water as well as with ME.

The viscosity B-coefficients give us quantitative values of ion-solvent interactions. But, we do not yet have an unambiguous method to divide the B-coefficients into their ionic values in all solvents. We have successfully used  $\text{Bu}_4\text{NBPh}_4$  as the "reference electrolyte" for the division of the viscosity B-coefficients in all our calculations. However, we lack sufficient data from different solvents to arrive at a definite conclusion about its validity and applicability. It is desirable to use various methods for this purpose and determine reasonably consistent ionic B-values.

Similarly, different methods may be used to find out the limiting ionic conductances from the limiting equivalent conductances of the electrolytes. Again, we have calculated the limiting apparent molar isentropic compressibilities of some electrolytes on the assumption that the limiting apparent molar isentropic compressibility of  $\text{BF}_4^- = 0$ . Although our assumption seems to be reasonable, proper evaluation of such properties would be of great help in determining ion-solvent interactions.

Solvation phenomena are very complex in nature. There are strong electrical forces between the ions and solvents and it is not really possible to separate them all.

Nevertheless, by using careful judgement, valid conclusions can be drawn in many cases from conductivity, viscosity, apparent molar volume and apparent molar isentropic compressibility measurements, relating to the structure and order of a system.

More extensive studies of the various thermodynamic and transport properties of the electrolytes will be of immense help in understanding the nature of ion-solvent interactions and the role of solvents in different chemical processes.

Thermodynamic studies do not directly address questions related to molecular scale features. They may only furnish some striking features of concentration or composition dependence that might reasonably be associated with important changes in the patterns of molecular interaction or aggregation. Perhaps we need to gather a lot of experimental data of a particular solvent and construct an appropriate model, incorporating the solvent's different modes of behaviour with a variety of electrolytes and non-electrolytes. The recent attempts at building such universal solvation models are in the right direction towards achieving this.

We may also need to carry out large scale computer simulations on a wide variety of solvents using such models and test their validity with the available experimental data. Such molecular modeling techniques may go a long way in updating our theoretical knowledge. They will also offer the chemists an inexpensive tool to conduct a host of experiments that may normally involve very expensive equipment.