

CHAPTER IX

CONCLUDING REMARKS

Symmetrical tetraalkylammonium and alkali metal salts show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions has come from studies on various thermodynamic properties e.g., apparent molal volumes, adiabatic compressibilities, heat capacities etc. as well as on transport properties e.g., conductance, viscosity and transference numbers. We therefore determined the thermodynamic and transport properties of some tetraalkylammonium and alkali metal salts in N,N-dimethylacetamide and its aqueous binary mixtures from the measurements of their viscosities, conductances, apparent molal volumes and adiabatic compressibilities. Raman spectral investigations of some alkali metal salts have also been attempted since these are potentially capable of yielding more precise information on the nature of interactions taking place in solutions. Excess properties of DMA + FA, DMA + DMF and DMA + EE systems were also studied, at three different temperatures. The measurements were analyzed with the appropriate equations and interpreted. The findings are summarized as follows.

In DMA, conductance and viscosity studies indicate that tetraalkylammonium bromide salts and the investigated alkali metal salts remain slightly associated in solutions. Lithium, sodium and potassium ions found to be significantly solvated while the tetraalkylammonium ions remain scarcely solvated in this medium. The viscosity of the solvent is greatly modified with the presence of all these ions

investigated here with the exception of the bromide ion. From the compressibility data we find that the lithium salts studied here exhibit appreciable ion-ion interaction in *N,N*-dimethylacetamide and the lithium ion is solvated through electrostriction of solvent molecules around the ions. The comparatively larger size anions show greater electrostatic solvation in this medium in contrast to electrostriction effect where smaller size anions predominate over others. The large tetraalkylammonium ion accommodate the solvent molecule inside the space between the alkyl chain attached to the nitrogen atom. In other words solvent molecules penetrate into these alkyl chains. For BPh_4^- ion neither electrostriction nor penetration of solvent molecules seems to be important. BF_4^- ions remains largely unsolvated.

Analysis of excess properties of the three systems indicate that in the DMA + FA system, strong heteroassociation is present through multiple hydrogen bonding between the polar groups of unlike molecules. On the other hand, there is weak dipole-dipole interaction and a slight structure-breaking effect in the DMA + DMF mixture as observed from the experimental data. In DMA + EE mixture, due to the presence of the highly polar ether group in 2-ethoxyethanol molecule, the hydrogen bonding interaction is playing a predominate role over the dispersion and other forces that are likely to be operative in non-aqueous solvent mixtures.

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 Bu_4NBPh_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 moving 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.