CHAPTER I

SCOPE AND OBJECT OF THE RESEARCH

Fundamental research on non-aqueous electrolyte solutions has catalysed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives, and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success.[1-2] Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photoelectrochemical cells, electromachining, etching, polishing, and electrosynthesis. In spite of wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions.[3] The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction.[2(b), 4]

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes is significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes.[5]

1.1 CHOICE OF THE MAIN SOLVENT USED

The study of alkoxyethanol, in general, is of interest because of their wide use as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastic products.

In recent years, 2-methoxyethanol (ME) – commonly known as methyl cellosolve – has drawn much attention as a solvent medium for various electrochemical investigations as well as for various industrial processes.[6,7] It figures prominently in the surface coating industry and also as an anti-freeze agent in the petroleum industry. It is an amphiprotic dipolar solvent of low dielectric constant (ϵ =16.94 at 298.15 K)[7] with large dipole moment (μ =2.36 D).[8] ME could be considered as a moderate Lewis acid,[9] and is a probable solvent for anions through its hydrogen-bonding network and dipole-induced reactions. It also has unique solvating properties associated with its quasiaprotic character.[10]

Even though ME has drawn much focus in recent years as a solvent for electroanalytical investigations,[11-21] still more studies on the electrolytic behaviour in this non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on ME to study the chemical nature of the structure of ions and their mutual and specific interactions with solvent molecules by studying the transport and thermodynamic properties of some selected electrolytes in ME.

1.2 SCOPE OF THE WORK

The object of the present work is therefore to elucidate the nature of various interactions of some common alkali and other important salts such as tetraphenylarsonium chloride (Ph_4AsCl), tetraphenylphosphonium chloride (Ph_4PCl), tetraphenylphosphonium bromide (Ph_4PBr), tetraphenylarsonium picrate (Ph_4AsPic), etc., in non-aqueous solvents having low dielectric constants such as 2-methoxyethanol (ε=16.94 at 298.15 K),[7] and 1,2–dimethoxyethane (ε= 7.08 at 298.15 K),[22] from volumetric, viscometric, conductometric, interferometric and FT-Raman spectral measurements. The available data have been utilised to examine the solvation phenomena of ions and ion-pairs in the non-aqueous solvents. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity.

Our further objective is to study the interaction between ME and a solvent of moderate dielectric constant, N,N-dimelthylacetamide (DMA), as well as ME and a solvent of very high dielectric constant, N-methylacetamide (NMA). More information about these two solvents, and 1,2-dimethoxyethane (DME) are given in Chapter 2.

1.3 METHODS OF INVESTIGATIONS

The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometry, viscometry, densitometry, ultrasonic interferometry and spectrophotometry to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in solvent viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The B - coefficients are also separated into ionic components by the "reference electrolyte" method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc, may be given.[17]

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

1.4 A SUMMARY OF THE WORK DONE

This dissertation consists of ten chapters, including the present one which is Chapter I.

Chapter II gives a general background to the area of the present work. It presents a brief review of significant work done earlier in the field of solvation phenomena and ion-solvent interactions. Beginning with a short note on the importance of solution chemistry, it discusses the thermodynamics of ion-pair formation, viscosity and conductance studies, ion-association together with single-ion conductance values, apparent and partial molar volumes and also ultrasonic velocity measurements, in more detail. It also contains a brief note on the recent research in these areas and ends with an account of the notable earlier works done on the solvents investigated, namely, 2-methoxyethanol, N-methylacetamide, N,N-dimethylacetamide and 1,2-dimethoxyethane.

Chapter III details the information about the various chemicals used, their methods of preparation and purification, and a brief description of the experimental techniques employed.

Chapter IV presents the thermodynamics of association processes of potassium picrate, potassium tetraphenylborate, tetrabutylammonium tetraphenylborate and tetraphenylarsonium picrate in 2-methoxyethanol at four different temperatures (288.15, 293.15, 298.15 and 308.15 K). The conductance data have been analysed by the 1978 Fuoss equation. From the ultrasonic velocity measurements, isentropic compressibility data and limiting apparent molar isentropic compressibilities have been calculated. The results are interpreted in terms of electrostriction of the solvent molecules and penetration of the solvent molecules into the larger solute ions, and their influence on the compressibility of the medium.

Chapter V deals with the thermodynamics of ionic association of tetraphenylarsonium chloride, tetraphenylphosphonium chloride, tetraphenylphosphonium bromide, lithium tetrafluoroborate, and sodium tetrafluoroborate in 2-methoxyethanol, at 288.15, 293.15, 298.15 and 308.15 K, known from their conductivity measurements. FT-Raman spectral analysis substantiates the moderate ion-pair formation of these electrolytes, as indicated by the conductance studies.

In Chapter VI, we report the ultrasonic velocities and isentropic compressibilities of the salts mentioned in Chapter V, in 2-methoxyethanol, at 288.15, 298.15 and

308.15 K. Apparent molar isentropic compressibilities are derived from these data supplemented by their densities. The results have been interpreted in terms of specific constitutional and structural factors of the solvent molecules and solute ions.

Chapter VII studies the solvation phenomena of sodium perchlorate, sodium tetrafluoroborate and sodium tetraphenylborate in 1,2-dimethoxyethane at 298.15 K, through conductance, viscosity, ultrasonic velocity and FT-Raman spectral measurements.

Chapter VIII compares the excess molar volumes, viscosity deviations and isentropic compressibility changes of N-methylacetamide and 2-methoxyethanol on the one hand, and, of N-methylacetamide and water, on the other. The observations made are interpreted in terms of intermolecular interactions and dispersion forces.

Chapter IX analyses the excess molar volumes, viscosity deviations and isentropic compressibility changes of N,N-dimethylacetamide and 2-methoxyethanol, on the one hand, and, of N,N-dimethylacetamide and water, on the other. The data obtained are interpreted in terms of specific/general interactions between the solvent molecules.

Chapter X contains some concluding remarks.

References

1. (a) Y. Marcus, *Ion Solvation*, Wiley-Interscience, Chichester, 1986.

   (b) Y. Marcus, *Ion Properties*, Dekker, New York, 1997.

2. (a) A. Marquez, A. Vargas, and P. B. Balbuena, *J. Electrochem. Soc.*, **45**, 3328, 1998.

   (b) A. F. D. Namor, M. A. L. Tanco, M. Salomon and J. C. Y. Ng, *J. Phys. Chem.*, **98**, 11796, 1994.

   (c) Y. Matsuda and H. Satake, *J. Electroanal. Chem.*, **127**, 877, 1980.

3. (a) O. Popovych and R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Wiley- Interscience, New York, 1981.

   (b) A. Chandra and B. Bagchi, *J. Phys. Chem. B.*, **104**, 9067, 2000.

   (c) G. Atkinson, R. Garnsey and M. J. Taft, in *Hydrogen Bonded Solvent Systems*, Eds. A. K. Covington and P. Jones, Taylor and Francis Ltd., London, 1968.

4. W. E. Waghorne, *Chem. Soc. Rev.*, 285, 1993.

5. (a) R. G. Bates, *J. Electroanal. Chem.*, **29**, 1, 1971.

   (b) K. Gunaseelan, S. Dev and K. Ismail, *Ind. J. Chem.*, **39A**, 761, 2000.

6. L. Tassi, *J. Chem. Soc.,Faraday Trans.* **89**, 733, 1993.

7. G. C. Franchini, A. Marchetti, M. Tagliazucchi,L. Tassi and G. Tosi, *J. Chem. Soc., Faraday Trans.*, **87**, 2583, 1991.

8. P. Buckley and M. Brochu, *Can.J.Chem*, **50**, 1149, 1972.

9. A. P. Kreshkov, N. T. Smolova, A. Veveris and B. Spince, *Zh.Ic.Khim.*, **51**, 1827, 1977.

10. D. Dasgupta, S. Das and D. K. Hazra, *J. Chem. Soc. Faraday Trans.*, **84**, 1057, 1988.

11. G. Roux, G. Perron and J. E. Desnoyers, *J. Solution Chem.*, **7**, 639, 1978.

12. A. Marchetti, E. Picchioni, L. Tassi and G. Tosi, *Anal.Chem.*, **61**, 1971, 1989.

13. D. Dasgupta, S. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **62**, 1246, 1989.

14. D. Nandi, S. Das and D. K. Hazra, *J. Chem. Soc., Faraday Trans. 1*, **85**, 1531, 1989.

15. D. Nandi and D. K. Hazra, *J. Chem. Soc., Faraday Trans. 1*, **85**, 4227, 1989.

16. B. Das and D. K. Hazra, *J. Chem. Eng. Data*, **36**, 403, 1991.

17. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470, 1992.

18. B. Das, P. K. Muhuri and D. K. Hazra, *Acoust. Lett.*., **18**, 69,1994.

19. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269, 1995.

20. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **68**, 734, 1995.

21. P. K Muhuri, B. Das and D. K. Hazra, *J. Phys. Chem. B.*, **101**, 3329, 1997.

22. E. Renard and J. C. Justice, *J. Solution Chem.*, **3**, 633, 1974.