CHAPTER I

SCOPE AND OBJECT OF THE WORK

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.[1-4] Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photochemical 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.

Apart from this, there lies a close resemblance of certain non-aqueous solvents with some biomolecules which help building up the larger part of the animal body. In particular solvents like tertiary amides offer great interest for biochemists because they are related to structural problems in molecular biology.[5] The results obtained from the study of different electrolytes in these solvents help us to understand the role and nature of interaction of biological macromolecules in living organism.

The proper understanding of ion-solvent interactions at a quantitative level is required for analyzing the different phenomena associated with non-aqueous solution chemistry.[6-8] An extensive study in aqueous, non-aqueous and mixed solvents makes one thing clear that due to the presence of ion-solvent interaction majority of solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes.[9,10]

In this context, it is apparent that the real understanding of the ion-solvent interactions is a difficult task as the aspect embraces a wide range of topics. But this dissertation would like to concentrate on the measurements of transpsort properties like viscosity and conductivity, spectroscopic properties like FT-Raman and FTIR along with such thermodynamic properties as apparent and partial molar volumes and apparent molar adiabatic compressibility.

1.1 CHOICE OF THE SOLVENTS USED

Solvents containing the amide functional group constitute an important tool in the interpretation of complex molecules of biological interest because they possess the very common in nature donor – acceptor – CO-NH – peptide bond and also display the property of self-association by the H-bond.[5]

N,N-dimethylacetamide (DMA), one of the members of tertiary amide series has drawn much attention as a solvent medium for various biochemical and electrochemical investigations in recent years.[5] It is a dipolar aprotic solvent with dielectric constant of 37.78 at 298.15K.[11] It also has unique solvating properties associated with its hydrogen-bonding network.[5] We have done a series of investigations on N,N-dimethylacetamide to study 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 this medium.

In our investigations we have included one unsubstituted amide formamide (FA) and a disubstituted amide N,N-dimethylformamide (DMF) as an organic component for the binary mixture with DMA. Formamide has a relatively high dielectric constant (ε = 109.5 at 298.15K)[11]. It is a dipolar protic solvent with a dipole moment of 3.73D at 298.15K.[11] On the other hand, DMF is a dipolar aprotic solvent with a quite large dipole moment (μ = 3.28D at 298.15K)[11] and a moderately high dielectric constant (ε = 37.5 at 298.15K)[11]. Due to the large dipole moment DMF has high solvating power with respect to a lot of organic and inorganic substances and is also miscible with almost all common polar and non-polar solvents. 2-ethoxyethanol, commercially known as 'cellosolve' is also used as a component for the binary mixture with DMA. The cellosolves can also form intramolecularly hydrogen-bonded five membered ring monomers.[12] The solvent has a density 0.9252 g.cm^{-3} and a refractive index 1.4057 at 298.15K.[13] In view of its property and structure, the 2-ethoxyethanol is often regarded as 'quasi-aprotic' solvent.[12] More information about these solvents are given in the chapters.

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 tetraalkylammonium salts in N,N-dimethylacetamide from volumetric, viscometric, conductometric, interferometric, FTIR and FT-Raman spectral measurements. Conductometric measurements of some alkali metal salts also have been done in aqueous binary mixture of N,N-dimethylacetamide. The available data have been utilized to examine the solvation phenomena of ions and ion-pairs in this non-aqueous solvent and its aqueous binary mixtures. 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 N,N-dimethylacetamide (DMA) and a protic solvent, formamide (FA), as well as dipolar aprotic solvent, N,N-dimethylformamide (DMF) and a quasi-aprotic solvent 2-ethoxyethanol (EE).

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.[14]

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 nine 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 works 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 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, N,N-dimethylacetamide, formamide, N,N-dimethylformamide and 2-ethoxyethanol.

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 conductance, density and ultrasonic sound velocity measurements and FT-Raman, FTIR spectral analysis of alkali metal salts in pure DMA at 298.15 K. The conductance data have been analysed by the 1978 Fuoss conductance equation. From the density and ultrasonic sound velocity measurements apparent molar volumes (ϕ_v) and limiting apparent molar volume (ϕ^o_v), apparent molar adiabatic compressibility (ϕ_k) and its limiting value (ϕ^o_k) have been calculated. The results are interpreted in terms of ionic association of these salts and electrostriction of the solvent molecules and their influence on the compressibility of the medium.

Chapter V deals with the electrical conductances and viscosities of some tetraalkylammonium and alkali metal salts in pure DMA at 298.15K. The viscosity data have been analysed by the Jones-Dole equation to evaluate the viscosity B-coefficients of the electrolytes. The densities and ultrasonic sound velocities of the salts and solvent have been mentioned at 298.15K. Apparent molar volumes (ϕ_v) and apparent molar adiabatic compressibilities (ϕ_k) are derived from these data supplemented by their densities and sound velocities. The limiting values ϕ^o_v and ϕ^o_k and the experimental slopes S_v and S_k have been interpreted in terms of ion-solvent and ion-ion interactions respectively. Use has been made of the non-thermodynamic, so called extrapolation method to split the limiting apparent molar volumes into ionic contributions.

Chapter VI describes the studies on the conductances of alkali metal salts in aqueous binary mixture of DMA at 25°C. The data have been analysed by the 1978 Fuoss conductance equation and the characteristic parameters Λ^o, K_A and R have been evaluated. The single-ion conductances have been determined using the "reference electrolyte" method.

Chapter VII describes conductivity, viscosity, density and ultrasonic sound velocity measurement of some tetraalkylammonium salts in aqueous binary mixture of DMA at 298.15K. Various thermodynamic parameters derived from these measurements are interpreted in terms of ion-ion and ion-solvent interactions.

Chapter VIII analyses the excess molar volumes, viscosity deviations of N,N-dimethylacetamide and formamide, on the one hand, and, of N,N-dimethylacetamide and N,N-dimethylformamide, on the other. The chapter also includes isentropic compressibility, density, viscosity, intermolecular free length, acoustic impedance molar sound speed and some of their respective excess properties in the binary mixtures of N,N-dimethylacetamide with 2-ethoxyethanol. The data obtained are interpreted in terms of specific/general interactions between the solvent molecules.

Chapter IX contains some concluding remarks.

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