PREFACE

Scope and Object of the work:

The majority of reactions that are of chemical or biological interest occur in solution. It was previously believed that the solvent merely provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realised only recently as a result of extensive studies in aqueous and non-aqueous solvents. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated[1].

Inspite of vast collections of data on the different electrolytic and non-electrolytic solutions in water, the structure of water and the different types of interactions water undergoes with electrolytes are yet to be properly understood. However, the studies on properties of aqueous solutions have provide sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic-structure, ionic-mobility and common ions on the properties of aqueous solutions and a host of other properties[2,3]. Nevertheless, during recent years, there has been an increasing interest in the behaviour of electrolytes in non-aqueous and mixed solvents with a view to investigating ion-ion and ion-solvent interactions under varied conditions. However, different sequence of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open new vistas for physical chemists, and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry[4].

We are mainly interested in the studies of the ion-solvent interactions as they are the controlling forces in dilute solutions where ion-ion interactions are absent. Changes in these ion-solvent interactions on transfer of electrolytes between solvents are small but are sufficiently large to cause dramatic changes in chemical reactions involving ions. These 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 the extraction[5]. The importance of ionic hydrations in biochemistry and biophysics has been stressed[6].

The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Meck[7], Franks[8,9], Popovych[10], Bates[11,12], Parker[13,14], Criss and Salomon[15] and others[16-19]. The ion-ion and ion-solvent interactions have been subject of wide interest as apparent from the discussions of Faraday Transactions of the Chemical Society[19].

The mixed and non-aqueous solvents are increasingly used in chrometography, solvent extraction, in the elucidation of reaction mechanisms, in preparing high density batteries, etc.

The proper understanding of the ion-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents and thus pave the way for the real understanding of the different phenomena associated with solution chemistry. Estimates of ion-solvent interactions can be had thermodynamically and also from the measurements of partial molal volumes, Viscosity B-coefficients, limiting conductivity of ions and compressibility studies.

However, single ion-values cannot be obtained thermodynamically. Various theoretical and semi-empirical extra-thermodynamic assumptions have been made to estimate the single ion values.

The measurements of transference numbers of ions can give an unequivocal method of determination of the limiting conductivity of ions. Unfortunately, transference measurements are only few and the 'reference electrolyte' method is used in most cases. The single ion values enable us to determine the solvation number of ions.

Similarly, Viscosity B-Coefficients can be apportioned using the 'reference electrolyte' method.

Estimates of single ion values have enable us to refine our models of ion-solvent interactions. The acceptable values of the ion-solvent interactions would enable the chemists to choose solvents that will enhance (i) the rates of chemical reactions, (ii) the solubility of minerals in leaching operations or reverse the direction of equilibrium reactions etc.

It is thus apparent that the real understanding of the ion-solvent interactions is difficult as well as a challenging task. The aspect embraces a wide range of topics but we concentrated only on the measurements of transport properties like Viscosity, Conductivity and Compressibility.

Attempts have been made to determine the single ion values by the use of available methods and elucidate the various aspects of ion-solvent interactions.

These are described in the subsequent chapters.

Summary of the Works done:

The dissertation is divided into seven chapters.

The first chapter contains a fairly comprehensive and upto date review of the works done on the viscosity, conductivity and compressibility of electrolytes in aqueous and non-aqueous solvents.

The importance and utility of the studies on viscosity, conductivity and compressibility in the determination of ion solvation i.e. ion-solvent interactions have been stressed. Critical evaluation of the different methods of obtaining the single ion values and their implications have been made.

The different experimental techniques utilised in obtaining the results presented in the dissertation have been described in the second chapter.

The relative viscosities of solutions of tetraalkylammonium bromides and iodides in dimethylsulphoxide have been measured at 298, 308 and 318K. The experimental results have been analyzed using Jones-Dole equation. Ionic Viscosities B-Coefficients for the tetraalkyl salts have been analyzed on the basis of Einstein equation and structural contributions. Comparison of the ionic B-Coefficients based on Krumgalz's method has also been made. Transition state parameters for viscous flow have also been determined. These are described in chapter three of the dissertation.

In the fourth chapter, we describe the determination at 298, 308 and 318K of the relative viscosities of solutions of tetraalkylammonium chlorides, bromides and iodides, Sodium iodide and Sodium tetraphenylborate in DMSO + H_2O mixtures (20% - 100 wt.% of DMSO). The experimental results have been analyzed in the same way using Jones-Dole equation. The ionic B-Coefficients have been determined using the 'reference electrolyte' Bu_4NBPh_4. The results have been interpreted in the same way as given in the previous chapter.

Conductance values of the tetraalkylammonium halides, Sodium iodide and Sodium tetraphenylborate have been measured in DMSO + H_2O mixtures (20%, 40%, 60% and 80% by wt of DMSO). The results have been analysed using Shedlovsky's equation, Fuoss-Onsager equation and Fuoss (1978) equations. The limiting equivalent conductances of the electrolytes and the association constants have been determined. The limiting conductance values of the single ions have been determined using the 'reference electrolyte' Bu_4NBPh_4. The results have been analysed in terms of ion-solvent interactions and structural changes. These are described in Chapter V.

Compressibility measurements of the tetraalkylammonium halides and the related electrolytes in DMSO + H_2O mixture have been made. The compressibility values of the solvent mixtures and their electrolytic solutions provide the values of solvation numbers of the electrolytes. Efforts have been made to determine the solvation number of the ions using the 'reference electrolyte Bu_4NBPh_4 ' . These form the subject matter of chapter six of the thesis. The dissertation ends in Chapter VII with some concluding remarks.

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