PREFACE

Scope and object of the work

The solution properties have always been of interest to physical chemists but in recent years there has been an unprecedented interest in solution chemistry by physical organic chemists, inorganic chemists, electrochemists and most notably by biochemists. The interest stems from the fact that the majority of reactions that are of chemical, electrochemical and biological importance 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, non-aqueous and mixed 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 that water undergoes with electrolytes are yet to be properly understood. However, the studies on the properties of aqueous solutions have provided 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 have been 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. Influence of these ion-solvent interactions on transfer of electrolytes between solvents is small, but 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 syntheses, studies of reaction mechanisms, non-aqueous battery technology and extraction[5]. The importance of ionic hydration 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], Mercus[16] and others[17-23]. The ion-ion and ion-solvent interactions have been the subject of wide interest as apparent from the discussions of Faraday Transactions of the Chemical society[24].

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 have the way for the real understanding of the different phenomena associated with solution chemistry. Estimates of ion-solvent ineractions can be obtained thermodynamically and also from the measurements of viscosity B-coefficients, limiting ionic conductivities etc.

However, single-ion values can not be obtained thermodynamically. Therefore, various theoretical and semi-empirical extra thermodynamic assumptions have been made to estimate these values.

It is thus apparent that the real understanding of the ion-solvent interactions is a difficult task. The aspect embraces a wide range of topics but we concentrated only on the measurements of transport properties like viscosity and conductivity along with such thermodynamic properties as apparent and partial molal volumes and apparent molar adiabatic compressibility.

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

These are deseribed in the subsequent chapters.

Summary of the works done

Acetonitrile methanol and its binary mixtures have been chosen as the solvent system in the present study.

The solvent acetonitrile has drown attention in recent years because of its use in technologycal applications namely in battary system and plating techniques[25,26].

The present dissertation has been divided into ten chapters.

Chapter I forms the background of the present work. After presenting a brief review of notable works in the field of ion-solvent interactions, such properties as viscosity, conductance, apparent and partial molal volumes have been discussed in details. The importance and utility of the various methods in the determination of ion-solvent interactions are stressed. Critical evaluations of the different methods of obtaining the single-ion values and their implications have been made. The solvent properties are then discussed, stressing the importance of such work.

In chapter II the discribes the experimental techniques for obtaining the results presented in the dissertation have been described.

In chapter III describes the determination of the apperent and partial molal volumes of six symmetrical tetraalkylammonium bromides in acetonitrile at 298.15, 308.15 and 318.15 K. The apperent molal volumes have extraporated to zero concentration to obtain the limiting values at infinite dilution. The infinite dilution partial molar expansibilities have also been calculated from the temperature dependence of the limiting apparent molar volumes. The variation of ϕ_v^0 with tempera-ture has been explained from the viewpoint of ion-solvent interactions.

In chapter IV the viscosity of solution of six symmetrical tetraalkylammonium bromides (Et$_4$NBr to Hep$_4$NBr) and tetrabutylammonium tetraphenylborate (Bu$_4$NBPh$_4$) have been measured at 288.15, 298.15, 308.15 and 318.15 K. The data have been analysed by the Jones-Dole equation[27] to evalute the viscosity B-coefficients of the electrolytes. The resulting B-coeffi-cient[28] and its dependence on temperature provide useful information regarding ion-ion and ion-solvent interactions. Ionic B-coefficients have been analysed on the basis of Einstein's equation[29].

In Chapter V densities and viscosities have been measured for the binary mixtures of acetonitrile and methanol as a function of mole fraction at temperatures of 298.15, 308.15, and 318.15 K. The excess molar volumes V^E derived from the experimental density data and the deviation of the viscosity of mixtures from the ideal mole fraction rule $\Delta\eta$ are negative at all temperatures investigated. The V^E and $\Delta\eta$ values have been fitted to a Redlich-Kister-type polynomial relation[31] to estimate the coefficients and standard deviations. The results are used to interpret the nature of interactions.

In Chapter VI the apparent molar volumes of six symmetrical tetraalkylammonium bromides, R_4NBr (R ethyl to heptyl) have been determined in methanol + acetonitrile binary mixtures (containing 0.00, 0.20, 0.40, 0.60 and 0.80 mole fractions of acetonitrile). Use has been made of the nonthermodynamic, so-called extrapolation method to split the limiting apparent molar volumes into ionic contributions. The results have been interpreted in terms of ion-ion and ion-solvent interactions.

In Chapter VII isentropic compressibility of some symmetrical tetraalkylammonium bromides have been masured in acetonitrile + methanol mixtures as a function of mole fraction at 298.15 K. The isentropic compressibility K_s were calculated by useing the Laplace equation.

In chapter VIII describes the electrical conductance measurements of six symmetrical tetraalkyllammonium bromides (Et_4NBr to Hep_4NBr), and tetrabutylammonium tetraphenyl borate (Bu_4NPh_4B) in methanol, acetonitrile, and methanol + acetonitrile binary mixtures at 298.15 K. The conductance data have been analysed by the Fuoss conductance-concentration equation[30] in terms of the limiting molar conductance (Λ^0), the association constant (K_A), and the distance of closest approach of ions (R). Single ion conductivities have been determined on the basis of tetrabutylammonium tetraphenylborate as the reference electrolyte. The results have been interpreted in terms of ion-ion and ion-solvent interactions.

In Chapter IX the viscosities of solutions of tetraethylammonium bromide (Et$_4$NBr), tetrapropylammonium bromide (Pr$_4$NBr), tetrabutylammonium bromide (Bu$_4$NBr), tetrapentyl ammonium bromide (Pen$_4$NBr), tetrahexylammonium bromide(Hex$_4$NBr), tetraheptylammonium bromide (Hep$_4$NBr), and tetrabutylammonium tetraphenylborate (Bu$_4$NBPh$_4$) have been measured at 298.15, 308.15 and 318.15 K in methanol + acetonitrile binary mixtures (containing 0.00, 0.20, 0.40, 0.60 and 0.80 mole fractions of acetonitrile). The data have been analyzed by the Jones-Dole equation[27] to evaluate the viscosity B-coefficients of the electrolytes. The resulting B-coefficient[28] and its dependence on temperature provide useful information regarding ion-ion and ion-solvent interactions. Ionic B-coefficients have been analysed on the basis of Einstein's equation[29].

The dissertation ends with some concluding remarks in chapter X.

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