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].

In spite 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 opened 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 ion-solvent interactions as these 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 have also 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 pave the way for the real understanding of the different phenomena associated with solution chemistry. Estimates of ion-solvent interactions can be obtained thermodynamically and also from the measurements of viscosity B-coefficients, limiting ionic conductivity 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 solubilities, free energies of solution and free energies of transfer.

Attempts have been made to determine the single-ion values by the use of available methods and to elucidate the various aspects of ion-solvent interactions. Vibration spectroscopy has also been applied to study the ion-solvent interactions of some alkaline earth metal salts in non-aqueous solvent medium.

Solvent-solvent interactions also play a vital role in solution chemistry. An effort has been made here to focus some light on the solvent-solvent interactions by measuring excess thermodynamic properties with the help of densimetry and viscometry at different temperatures.

These are described in the subsequent Chapters.

Summary of the work done

Propylene carbonate (PC) and its binary mixtures with methanol have been chosen as the solvent system in the present study.

The present dissertation has been divided into nine chapters.

Chpater 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 solubility and free energy of solution, viscosity and conductance 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 different experimental techniques for obtaining the results presented in the dissertation have been described.

Chapter III entails the studies on the solubilities of some alkali metal salts, tetraphenylarsonium chloride and tetraphenylphosphonium bromide in PC at 25°C. Most of the alkali metal halides barring a few are scarcely soluble in PC and thus the more conventional methods like conductometry and viscometry can hardly be applied to understand the ion-solvent interactions of these electrolytes in this solvent medium. Solubilities for these salts have been measured by using ion selective electrode technique and the corresponding free energies of solution have been determined. Combination of these values with those in water has resulted the free energies of transfer of the electrolytes from water to PC. Transfer activity coefficients or medium effects have also been computed from their solubility products in water and in the non-aqueous solvent. Single ion transfer functions have been evaluated by making use of extrathermodynamic assumptions involving "reference electrolyte" method.

Chapter IV comprises two parts. Part A describes the viscosities of some tetraalkylammonium bromides in propylene carbonate at different temperatures. Viscosity data have been analysed by the Jones-Dole equation for unassociated electrolytes[25]. Single ion values have been estimated by using the "reference electrolyte" method. In Part B, the conductance measurements have been reported for the tetraalkylammonium bromides in PC at 25°C. Conductance data have been analysed by the 1978 Fuoss conductance equation[26]. Single ion equivalent conductances at infinite dilution have been evaluated by using the "reference electrolyte" method.

Chapter V describes the determination of viscosities and electrical conductances of some tetraphenyl salts in PC. Viscosities have been measured at 25, 35 and 45°C and the B coefficients have been calculated. Conductance data have been analysed by the Fuoss conductance equation[26]. Single ion values have also been evaluated. Results are discussed in terms of the interactions of the ions with the solvent medium.

Excess molar volumes (V^E), excess viscosities (η^E) and excess molar free energies of activation of flow (G^{*E}) have been determined for four sets of binary mixtures of propylene carbonate with methanol, 2-methoxy ethanol, 1,2-dimethoxyethane and tetrahydrofuran at 25, 35 and 45°C and the results has been described in Chapter VI. The excess functions have been discussed from the view point of intermolecular interactions. The proper understanding of these interactions would enable us to extract useful information from the studies of ion-solvent interactions of electrolytes in these solvent mixtures.

Chapter VII describes the studies on the electrical conductances of some tetraalkylammonium bromides, R_4NBr (R = Me to Hep). $NaBPh_4$ and Bu_4NBPh_4 in PC + methanol mixtures at 25°C. The data have been analysed and the characteristic parameters, Λ_o, K_A and Walden products have been evaluated. The single ion conductances have been determined using the "reference electrolyte" method. Results have been discussed in terms of the structural changes of the solvent mixtures.

In Chapter VIII infra-red and Laser-Raman spectroscopic measurements have been reported for some alkaline earth metal perchlorates in PC. The results have been interpreted in terms of ion-solvent interactions with the PC molecules.

The dissertation ends with some concluding remarks in Chapter IX.

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