PREFACE

Scope and Object of the Work

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are well-recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck[1], Franks[2], Popovych[3], Bates[4,5], Parker[6,7], Criss and Salomon[8], Mercus[9] and others[10-12]. The ion-ion and ion-solvent interactions have been subject of wide interest as apparent from recent Faraday Transactions of the chemical society[13].

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 signicicance 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 the 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[14].

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 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 preperties[15,16]. 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[17].

We are mainly interested in the studies of ion-solvent interactions as they are 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[18] and extraction[19]. The importance of ionic hydration in biochemistry and biophysics has been stressed[20].

The proper understanding of the ion-solvent intaractions 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 real understanding of the different phenomena associated with solution chemistry. Estimate of ion-solvent interactions can be obtained thermodynamically and also from the measurements of partial molar volumes, viscosity B- co-efficients and conductivity studies.

Estimates of single-ion values enable us to refine our models of ion-solvent interactions. Acceptable values of 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 a difficult task. The aspect embraces a wide range of topics but we concentrated on the measurements of transport properties like viscosity and conductivity as well as of thermodynamic properties such as apparent molal volume and apparent molal adiabatic compressibility studies.

These are described in subsequent chapters.

Summary of the Works done

Tetrahydrofuran (THF), 1,2 dimethoxyethane (DME) and their aqueous mixtures have been chosen as the solvent system in the present study.

Both these solvents are ether. THF is a cyclic ether and DME is an open-chain ether. They have a similarity with each other with respect to their physical properties.

Tetrahydrofuran (THF) and 1,2 dimethoxyethane (DME) are commercially known as ' Cellosolves ' being used extensively as a solvating agent for Celluiose. THF, a low permittivity (ϵ = 7.58) has also been found its probability of application in high energy batteries and organic syntheses as manifested from the physico-chemical studies in this medium [21,22]. 1,2 dimethoxyethane (DME) is used now-a-days as an electrochemical solvent in non-aqueous battery electrolyte and also as solvents for the preparation and reaction of organoalkaline earth compounds [23].

The present dissertation has been divided into eight 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 conductance, viscosity, apparent molal adiabatic compressibility have been 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, streesing the importance of such work.

Chapter II describes the conductances of the tetra-alkylammonium bromides, R_4NBr ($R = C_4H_7^-$ to $C_7H_{15}^-$), $LiBF_6$ and $LiAsF_6$ in tetrahydrofuran (THF) at 25°C. The conductance data have been analysed using the Fouss-Kraus Theory[24] yielding values for the ion-pair and triple-ion formation constants.

Chapter III entails the studies on relative viscosity of tetraalkylammonium bromides in tetrahydrofuran (THF) at 25 and 35°C. The experimental results have been analysed by using Jones-Dole[25], Moulik[26], Breslau[27] and Vand[28] equations.

Chapter IV describes the determination of the apparent and partial molal volumes of some tetraalkylammonium bromides in tetrahydrofuran (THF) and 1,2 dimethoxyethane at 25, 30, 35, 40, and 45°C. The limiting apparent molal volumes (ϕ_V^o) and experimental slopes (S_V^*) 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 molal volumes into the ionic contributions. The variation of ϕ^o_V with temperature has been explained from the view point of ion-solvent interactions.

Excess molar valumes (V^E), excess viscosities (η^E) and excess molar free energies of activation of flow (G^{*E})

have been reported for tetrahydrofuran + water and 1,2 dimethoxyethane + water mixtures at 25, 35 and 45°C in chapter V. 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 viscosities and conductances of electrolytes in THF and THF + H_2O mixtures.

Chapter VI describes the studies on the conductances of alkali metal chlorides and bromides in Tetrahydrofuran + water mixtures (20, 40, 60 and 80 wt% of THF) at 25°C. The data have been analysed by the 1978 Fouss conductance equation and the characteristic parameters, Λ^o, K_A and R have been evaluated. The ionic Walden products have been determined and their variations with solvent compositon discussed.

In Chapter VII, adiabatic compressibility data have been reported for some alkali metal chlorides and bromides in Tetrahydrofuran + water mixtures at 25°C. The compressibility data have been analysed in terms of the limiting apparent molal adiabatic compressibility (ϕ_k^o) and the experimental slope (S_k) and the results reveal the existance of solute-solvent and ion-ion interactions in these solvent mixtures.

The dissertation ends with some concluding remarks in Chapter VIII.

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