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 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 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 unfamilier 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 bio chemistry and biophysics has been stressed[6].

The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarised by Meck[7], Franks[8,9], Popovych[10], Bates[11,12], Parker[13,14], Criss and Salomon[15] and others[16-18]. 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 chromatography, 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 molar volumes, viscosity B-coefficients and limiting ionic conductivity 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 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.

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

2-methoxy ethanol (ME), 1,2-dimethoxy ethane (DME) and aqueous mixtures of 2-methoxy ethanol have been chosen as the solvent system in the present study.

Both ME and DME are known[20] to be intermolecularly hydrogen bonded, ME (ϵ = 16.93)[21] having the cis conformation and DME trans as preferable conformation. DME with $\epsilon = 7.075$[22] and $\mu = 1.71D$[23] is an aprotic etheral solvent. ME $[\mu = 2.18D]$[24] is an alkoxyethane thus exhibiting properties of alcohols and ethers at the same time. The solvent is expected to be intermediate between EG and DME in behaviour. It is potentially a protic solvent due to -OH group present and at the same time intramolecular hydrogen bonding would impart some aprotic character to it, restricting the availability of the hydroxyl proton and thus "quasi-aprotic" ME is expected to show some properties characteristic of aprotic solvents.

The present dissertation has been divided into eight chapters.

Chapter I forms the background of the present works. After presenting a brief review of notable works in the field of ion solvent interactions, the discussion centres around the viscosity B-coefficients, its division and temperature dependence. The apportioning of B-coefficient into individual ionic contributions, leds to a great deal of controversy, since no thermodynamic procedure could realise such quantities. Detail discussions on the relative merits and demerits on the various assumptions employed time to time have been presented. The importance and utility of the viscosity and conductivity methods in the determination of 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 solvent properties was then discussed, stressing the importance of such work.

In Chapter II the different experimental techniques in obtaining the results presented in the Dissertation have been described.

Chapter III entails the studies on viscosity B-coefficients of tetraalkylammonium bromides in 2-methoxy ethanol (ME) at 25°C and 30°C. The experimental results have been analysed using Feakins et al equation[25] instead of Jones-Dole equation[26] because of the strong association of the electrolytes in this medium. The B-coefficients of the total electrolytes have been apportioned into individual ionic contributions using the 'reference electrolytes' viz. Bu_4NBPh_4 and Bu_4NBBu_4. Ionic B-coefficients have also been analysed on the basis of Einstein's equation and structural contributions. Ion-solvent interactions have also been discussed in terms of transition state treatment of viscous flow.

Chapter IV described the determination at 25°C and 30°C of the relative viscosities of solutions of tetraalkylammonium bromides, sodium bromide and sodium tetraphenyl borate in ME + water mixtures. The experimental results have been analyzed by Jones-Dole and Feakins et al equations[25]. The thermodynamic parameters of the salts have been determined using the transition state treatment and the temperature coefficient measurements. The ionic B-coefficients and other single ion parameters have been determined by appropriate division of the 'reference electrolyte'

Bu_4NBPh_4. The results have been discussed in terms of structural changes of the solvent mixtures.

Chapter V describes the studies on the conductances of tetraalkylammonium bromides in 2-methoxy ethanol (ME) at 25°C. The data have been analysed by means of the Fuoss conductance equation[27] in terms of the limiting molar conductivity, Λ^o, the association constant, K_A, and the association distance R. The limiting ion conductances have also been calculated from Λ^o-values of the 'reference electrolytes' Bu_4NBBu_4 and Bu_4NBPh_4 and the values compared with previous work on similar systems.

In Chapter VI conductance measurements have been reported for tetraalkylammonium bromides, R_4NBr ($R = C_2H_5-$ to $C_5H_{11}-$), sodium bromide and sodium tetraphenyl borate in 2-methoxy ethanol + water mixtures (20, 40, 60 & 80 wt% of ME) at 25°C. The data have been analysed by the Shedlovsky equation and also 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' Bu_4NBPh_4. The ionic Walden products have been determined and its variations with solvent compositions discussed.

Chapter VII describes the conductances of the tetraalkylammonium bromides, R_4NBr ($R = C_4H_9-$ to $C_7H_{15}-$) in 1,2-dimethoxy ethane (DME) at 25° C. The conductance data have been analysed using the Fuoss-Kraus theory[28] yielding values for the ion pair and triple ion formation constants.

The dissertation ends in Chapter VIII with some concluding remarks.

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