

A C K N O W L E D G E M E N T

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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 elucidated¹.

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 open new vistas for physical chemists, and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry⁴.

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 extraction⁵. The importance of ionic hydration in biochemistry and

biophysics has been stressed⁶.

The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Meck⁷, Franks^{8,9}, Popovych¹⁰, Bates^{11,12}, Parker^{13,14}, Criss and Salomon¹⁵, Marcus¹⁶ and others¹⁷⁻²³. 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 Society²⁴.

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 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 molal adiabatic compressibility.

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.

These are described in the subsequent chapters.

Summary of the works done

2-Methoxyethanol (ME) and its aqueous mixtures have been chosen as the solvent system in the present study.

ME is known to be intramolecularly hydrogen bonded²⁵, the predominant configuration is the gauche form. ME ($\mu = 2.18$)²⁶ is an alkoxyethanol thus exhibiting properties of alcohols and ethers at the same time. The solvent is expected to be intermediate between ethylene glycol (EG) and 1,2-dimethoxyethane (DME) in behaviour. It is potentially a protic solvent due to the presence of -OH group; at the same time intramolecular hydrogen-bonding would impart some aprotic character to it, restricting the availability of the hydroxy proton and thus "quasi-protic" ME is expected to show some properties characteristic of aprotic solvents.

The present dissertation has been divided into nine 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 and apparent molal adiabatic compressibility 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 viscosities, conductances and adiabatic compressibilities of some tetraalkylammonium perchlorates in 2-methoxyethanol. The conductance data have been analysed by the 1978 Fuoss conductance equation²⁷ in terms of the limiting molar conductivity (Λ°), the association constant (K_A) and the association distance (R); and the viscosity data by the Jones-Dole equation for associated electrolytes²⁸. The thermodynamic parameters of the salts have been determined using the transition-state treatment²⁹. The ionic

contribution to the limiting molar conductance, viscosity B coefficient and other thermodynamic parameters have been determined by making use of the "reference electrolyte" method. Ionic B-coefficients have been analysed on the basis of Einstein's equation³⁰ and structural contributions. The compressibility data have been analysed^{31,32} in terms of the limiting apparent molal adiabatic compressibility (ϕ_K°) and the experimental slope (S_K).

Chapter IV describes the determination of the apparent and partial molal volumes of some tetraalkylammonium bromides and perchlorates in ME at 25, 35 and 45°C. The limiting apparent molal volumes (ϕ_V°) and the 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 ionic contributions. The variation of ϕ_V° with temperature has been explained from the viewpoint of ion-solvent interactions.

In Chapter V viscosity, conductance and Laser-Raman spectroscopic measurements have been reported for alkali metal perchlorates in 2-methoxyethanol. Viscosity and conductance data have been analysed by the 1978 Fuoss Conductance equation²⁷ and the Jones-Dole equation for associated electrolytes²⁸, respectively. Single-ion values have been estimated by using the "reference electrolyte" method. The results of the Laser-Raman

spectroscopic measurements have been interpreted in terms of solute interference with the ME molecules.

Excess molar volumes (V^E), excess viscosities (η^E) and excess molar free energies of activation of flow (G^{*E}) have been reported for 2-methoxyethanol + water mixtures at 25, 35 and 45°C in Chapter VI. The excess functions have been discussed from the viewpoint 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 ME + H₂O mixtures.

Chapter VII describes the determination of viscosities of solutions of tetraalkylammonium perchlorates, R₄NClO₄ (R = Et to Bu), LiClO₄, NaClO₄, LiBF₄, LiAsF₆ and NaBPh₄ in ME + Water mixtures at 25, 35 and 45°C. The experimental results have been analysed by the Jones-Dole³³ and Feakins et al²⁸ equations. The thermodynamics parameters of the salts have been determined by using the transition state treatment of the relative viscosity²⁹. The ionic B-coefficients and other single-ion parameters have been determined by appropriate division of those values for reference electrolyte. The results are discussed in terms of structural changes of the solvent mixtures.

Chapter VIII describes the studies on the conductances of the salts (same as those used in Chapter VII) in ME + Water

mixtures at 25°C. The data have been analysed by the 1978 Fuoss conductance equation²⁷ and the characteristic parameters Λ° , K_A and R have been evaluated. The single-ion conductances have been determined using the "reference electrolyte" method. The ionic Walden products have been determined and their variations with solvent composition discussed.

The dissertation ends with some concluding remarks in Chapter IX.

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