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 realized 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 behaviors of electrolytes in non-aqueous and mixed solvents with a view to investigate 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 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 Solomon[15], Marcus[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 from 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 interactions can be obtained thermodynamically and also from the measurements of viscosity *B*-coefficients, limiting ionic conductivities etc.

However, single-ion values cannot 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 two important transport properties e.g., viscosity and conductivity of electrolyte solutions.

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-Ethoxyethanol (EE) and its binary aqueous mixtures have been chosen as the solvent system in the present study.

The present dissertation addresses the problem of solute-solvent and solute-solute interactions for some selected electrolytes in 2-ethoxyethanol and its mixtures with water using two well-established experimental techniques and has been divided into six chapters.

Chapter I forms the background of the present work. After presenting a brief review of the notable works in the field of ion-solvent interactions, conductivity and viscosity of electrolyte solutions have been discussed in details. The importance and utility of these methods for 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 a study on the electrical conductances of some symmetrical tetraalkylammonium and alkali metal salts (tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetraheptylammonium bromide (Hep_4NBr), sodium bromide (NaBr) and sodium tetraphenylborate ($NaBPh_4$) in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ^0), the association constant (K_A) and the association diameter (R). The ionic contributions to the limiting molar conductance have been estimated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte".

The analysis of the results provided important information on the ion-association and solvation behaviour of these electrolytes in 2-ethoxyethanol.

In Chapter IV the viscosity of solutions of some tetraalkylammonium bromide salts (Et_4NBr, Pr_4NBr, Bu_4NBr, Pen_4NBr and Hep_4NBr) have been measured in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The viscosity data have been analyzed by the Jones-Dole equation for the associated electrolytes to evaluate the viscosity *B*-coefficients of the electrolytes. The resulting *B*-coefficients along with their ionic contributions and their temperature dependences provide useful information regarding ion-ion and ion-solvent interactions in 2-ethoxyethanol.

Chapter V describes the studies on the conductances of solutions Et_4NBr, Pr_4NBr, Bu_4NBr, Pen_4NBr, NaBr and $NaBPh_4$ in EE-water mixtures containing 0.25, 0.50 and 0.75 mass fractions (w_1 = 0.25, 0.50 and 0.75) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ^0), the association constant (K_A) and the association diameter (R). The ionic contributions to the limiting molar conductance have been estimated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte". The ionic Walden products have been determined and their variations with solvent composition discussed.

In Chapter VI, the viscosities of solutions Et_4NBr, Pr_4NBr, Bu_4NBr, NaBr and $NaBPh_4$ in 2-ethoxyethanol-water mixtures containing 0.25, 0.50 and 0.75 mass fractions (w_1 = 0.25, 0.50 and 0.75) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K have been reported. The experimental results have been analyses by the Jones-Dole[25] and Feakins *et.* al[26]. The thermodynamic parameters of these electeolytes have been determined using the transition-state treatment of the relative viscosity[26]. The ionic *B*-coefficients and other single-ion parameters have been determined by appropriate division of those for the "reference electrolyte" Bu_4NBPh_4. The results were discussed in terms of structural changes of the solvent mixtures.

The dissertation ends with some concluding remarks in Chapter VII.

The solvent 2-ethoxyethanol (EE) and its importance

2-Ethoxyethanol belongs to a class of compounds commercially known as cellosolves. It is, in fact, the monoethyl ether of ethylene glycol. Hence, it is very likely to show physico-chemical characteristics midway between protic and dipolar aprotic solvents. Therefore, it is of much interest to study the behaviour of electrolytes in such solvent medium.

Simple consideration of molecular structures indicates that, due to the presence of electron repelling CH_3CH_2- group, 2-ethoxyethanol is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H atom of OH group makes 2-ethoxyethanol molecules less acidic than ethylene glycol and water, thus imparting a "quasi-aprotic" character to it. That is, it behaves as an amphiprotic dipolar solvent with low relative permittivity (ε =13.38 at 298.15 K)[27]. Moreover, it is completely miscible in water.

Studies on fundamental physico-chemical properties like density and dielectric constant alongwith isentropic compressibilities and heat capacities have been reported for 2-ethoxyethanol[28,29,30,31]. Density measurements on the 2-ethoxyethanol-water mixtures have been performed at 298.15 K by McKinley and Nibarger[32]. Later the Douheret[27, 31] group reported densities, dielectric constants and isentropic compressibilities for this mixed solvent media at 298.15 K. Excess apparent molal heat capacities and volumes of 2-ethoxyethanol in the water-rich region at different temperatures have been reported by Roux *et. al.*[29] and it has been shown that 2-ethoxyethanol behaves as a fairly typical polar nonelectrolyte in water.

In spite of the extensive use of cellosolves as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastic products[33, 34], the studies on the transport properties of electrolytes in these media and their mixtures with water have not stimulated much interest so far. However, the knowledge of transport properties of different electrolytes in these solvents is capable of indicating the potential usefulness of cellosolves in various technologies, *e.g.*, high-energy nonaqueous batteries, ion exchangers etc. The situation is somewhat better with the first homologue of this class, namely, 2-methoxyethanol. Extensive studies on the transport properties of various electrolytes have already been reported in pure 2-methoxyethanol as well as in its binary mixtures with water[35-44]. Unfortunately, such investigations in 2-ethoxyethanol and its aqueous mixtures are practically absent.

We have, therefore, devoted our attention to the study of the transport properties of some electrolytes in 2-ethoxyethanol and its aqueous binary mixtures.

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