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 (particularly solution thermodynamics) by physical organic chemists, inorganic chemists, electrochemists and most notably by bio-chemists. The interest stems from the fact that the majority of reactions that are of chemical, electrochemical and biological interest occur in solution. The importance of solvent effects on reaction rates and mechanisms, on the nature of ionic interactions in electrolytic solution and the conformational properties of proteins and other biologically important molecules has been extensively examined in aqueous, non-aqueous and mixed solvents.

It has been realised that the majority of the solutes are significantly modified by the solvents in general whereas the nature of the strongly structured solvents (like water) is drastically changed by the presence of solutes. The true understanding of the solution phase thus demands the proper understanding of the solute-solute, solute-solvent and solvent-solvent interactions from theoretical and experimental studies[2-4] using thermodynamics, kinetics, spectroscopic, electrochemical methods etc.

Studies on the properties of aqueous solutions have provided sufficient information on the dissociation constants of ligands and their complexes, the effects of variation of ionic structure, ion-mobility and common ions on the properties of aqueous solutions and a host of other properties. Still the problem of solute (ion)-solvent interactions has not been clearly understood (in view of our inadequate knowledge on the structure of water).

The essential drawback arises from the lack of absolute structure of liquid water in spite of tremendous amount of work done on the properties of water and aqueous solutions.

However, the recent development in the field of analytical chemistry in particular and other exigencies to understand specific molecular interactions (i.e. ion-ion interactions, ion-solvent interactions, H-bonding etc) led to the tremendous advancement in the study of different physico-chemical properties in non-aqueous and mixed solvents.

Different sequences of solubility, differences in solvating power and possibilities of chemical and 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[2].

Changes in the 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 diverse areas:-

i) In organic, inorganic synthesis and in analytical chemistry[3-5].

ii) In the elucidation of reaction mechanisms[3,6].

iii) In chromatography, solvent extraction and in the development of ion-exchangers for different purposes[3].

iv) In the development of non-aqueous battery technology[4,7,8].

v) In the processing of materials to recover metals from non-aqueous baths with low energy consumption[9,10].

vi) In processes involving salting in and salting out phenomena[11].

vii) In various biological processes[3].

The importance of ionic hydration in biochemistry and biophysics has also been stressed[12].

The most important and elusive aspect of the solution chemistry is the determination of 'single ion' thermodynamics or more particularly 'medium effect' of ions in mixed and non-aqueous solvents. Single ion values obtained by using empirical extra-thermodynamic assumptions enable us to refine our models of ion-solvent interactions and form the basis of explaining quantitatively the influence of the solvents (particularly on the reaction rates) and the extent of interactions of ions in solvents. These studies pave the way for the real understanding of the different phenomena associated with the solution chemistry. The medium effect can be used in

1) the establishment of a single, solvent independent scale for the activities of individual ions, in particular pH.

2) the formation of solvent independent series for the standard electrode potentials.

3) the evaluation of liquid junction potential at the interface of different solvents.

The applications and implications of the studies of reactions in non-aqueous and mixed solvents, ion-solvent interactions, medium effects have been summarised by different authors[2,3,10,12-17].

We have undertaken the study of some of these aspects which will be discussed in the subsequent chapters.

Summary of the work done

2-Methoxyethanol (ME), 1,2-dimethoxyethane (DME) and aqueous mixtures of 2-methoxyethanol and 1,2-dimethoxyethane have been chosen as the solvent system in the present study.

Both ME and DME are known[18] to be intermolecularly hydrogen bonded, ME ($\epsilon = 16.93$)[19] having the cis conformation[20] and DME as the trans preferable conformation. DME with $\epsilon = 7.075$ and $\mu = 1.71D$[21] is an aprotic etheral solvent. ME ($\mu = 2.18D$)[22] 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; 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 seven chapters.

Chapter I forms the background of the present work. After presenting a brief review of notable works in the field of ion-solvent interaction, the discussion centres around the acid-base equilibria in non-aqueous and mixed solvents. Critical evaluation 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.

Chapter II entails the studies on the dissociation constants for the reactions $AH^+ \rightleftharpoons A + H^+$ (where, A = 2,2′-bipyridine or 1,10-phenanthroline) in binary aqueous mixtures of 2-methoxyethanol and 1,2-dimethoxyethane. The results have been discussed in terms of solvent-basicity and ion-solvent interactions. The free energy of transfer of H^+ ions $[\Delta G_t^o(H^+)]$ in mixed solvents have been determined.

Chapter III describes the determination of the dissociation constant of benzoic acid in ME - H_2O and DME - H_2O mixtures from solubility, spectrophotometry[23] and conductometric[24] measurements. The pK values obtained by the above methods have been compared and its variations with solvent compositions discussed.

Chapters IV and V describe the studies on the dissociation constants of o-, m- and p- substituted benzoic acids. The free energies of transfer of benzoate ions have been evaluated. The discussion ends in Chapter V with some concluding remarks.

In Chapter VI conductance measurements are reported for picric acid in ME and DME and in their binary aqueous mixtures at 25°C. The data have been analysed by the Shedlovsky[25] equation and also by the 1978 Fuoss[26] conductance equation and the characteristic parameters Λ_0 and K_A have been evaluated. The variations of Walden products with solvent compositions have been discussed.

Finally, Chapter VII concentrates on the determination of thermodynamic transfer functions for some 1:1 electrolytes in 2-methoxyethanol and 1,2-dimethoxyethane at 25°C. The estimation of transfer functions for single ions using 'reference electrolyte' assumptions[27-31] have also been presented in this chapter.

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