PREFACE

Scope and Object of the work :-

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents were well-recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck[1], Franks[2,3], Popovych[4], Bates[5,6], Parker[7,8], Criss and Salomon[9] and others[10,11]. The ion-ion and ion-solvent interactions have been subject of wide interest as apparent from recent Faraday Transactions of the Chemical Society[12].

Studies on properties of aqueous solutions have provided sufficient information on the dissociation constants and thermodynamics of the ligands and their complexes, the effects of variation of ionic structure, ion-mobility and common ions on the properties of aqueous solutions and to predict fairly accurately the types of species present in solution when a solute is dissolved in water. However, comparatively little work has been done to obtain the same type of information about the nature of non-aqueous solutions.

Recently, the atomic energy projects have helped to stimulate the interest in co-ordination chemistry in non-aqueous and mixed-solvents, since often the key to a successful purification or seperation of the heavy metal ions involves complex formation and solvent extraction. Thus, information concerning the nature of the ionic species present in non-aqueous and mixed solvents is required for any fundamental understanding of the chemistry of these systems. The careful measurements which are necessary to understand how solute-solvent interactions vary with widely different dielectric constants and solvating abilities have become frequent only during the past few years[1].

The study of physico-chemical processes in non-aqueous and mixed solvents is useful from the point of view of phase studies involving binary, ternary and quaternary solvent systems which find application in various analytical techniques e.g., chromatography and extraction[2,3].

The mixed solvents are increasingly used in the elucidation of reaction mechanisms. Formerly, it was used to widen considerably the range of reactions[2]. The most important but elusive aspect of the solution chemistry is the determination of 'single ion' thermodynamics or more particularly 'medium effect' of ions (particularly of hydrogen ions) in mixed and non-aqueous solvents. This would form basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents and thus the way for the real understanding of the different phenomena associated with solution chemistry.

Since single ion-values can not be obtained thermodynamically, various theoretical and semi-empirical extra-thermodynamic attempts have been made. The use of extra-thermodynamic assumptions to estimate ion-solvent interactions is important both from theoretical and practical point of view. Estimates of free-energies of transfer for ions have enabled us to refine our models of ion-solvent interactions. Additionally, armed with acceptable values of free-energies of transfer Chemists can choose solvents that will enhance the rates of many chemical reactions, the solubility of minerals in leaching operations or reverse, the direction of equilibrium reactions and give new methods of processing metals such as Copper[7].

We are, however, interested in the study of the effects of the various solvents on the dissociation constants of weak acids and basis and their complexes. Compared to most organic solvents, the dielectric constant of water is comparatively large. One of the principal effects produced by adding a miscible organic solvent to water is the reduction of dielelectric constant and the change in coulombic interactions between ions.

For the reactions,

$$AH^+ \rightleftharpoons A + H^+ \qquad (1)$$

$$AH \rightleftharpoons A^- + H^+ \qquad (2)$$

$$AH^- \rightleftharpoons A^{2-} + H^+ \qquad (3)$$

it is possible to predict qualitatively the effect of addition of an organic solvent which lowers the dielectric constant.

The addition of the organic solvent means a change in the 'medium effect' due to change in acid-base character of the organic solvent. This undoubtebly changes the non-electrostatic contributions. It is, however, difficult to say qualitatively and quantitatively to what extent it affects the dissociation constants of the ligands. Measurements of the dissociation constants in various mixed solvents give us an idea regarding the non-electrostatic contributions in various solvents. Bates and Robinson[13] have shown an uniformity in the non-electrostatic contributions in the case of different methanol-water mixtures from the study of the dissociation constants of the various ligands.

Studies on the dissociation constants of ligands in different solvent may throw some light on the ion-solvent interactions as well as solvent basicity. Till recently only very qualitative idea regarding the non-electrostatic parts have been obtained in solvents like dimethyl sulphoxide (dmso), N,N'-dimethyl formamide(dmf) and formamide. Quantitative values are still lacking.

The kinetic studies provide the most powerful methods of investigating detailed reaction mechanisms. Though absolute informations are rarely obtained but the postulations of reaction mechanisms is of the great help in understanding and systematizing the study of an area of chemistry. The effect of solvents on the reaction kinetics is extensiveand varied.

The importance of spectral studies are enormous. The studies are not only helpful for assignments of spectral transitions and the nature of $n - \pi^*$, $\pi - \pi^*$ transitions etc they also provide us an approximate idea of solute solvent interactions.

It is apparent that the solution chemistry embraces a wide range of topics but we concentrated only on some of the aspects with the limited resources at our disposal. These are described in the subsequent chapters.

Summary of the work done :-

The dessertation consists of three chapters which are subdivided into several sections.

The section I of chapter I contains a fairly comprehensive and up-to-date review of the works done in the field of non-aqueous[1] and mixed solvents. The importance of the determination of the single ion thermodynamics have been stressed.

In the subsequent sections of chapter I, we have described our studies on the dissociation constants for the reactions

$AH^+ \rightleftharpoons A + H^+$ (where A = 2,2'-bipyridine or 1,10-phenanthroline) in different aquo-organic solvents like dmso + H_2O dmf + H_2O and formamide + water mixtures. The results have been discussed interms of solvent - basicity and ion-solvent interactions. The free-energy of transfer of H^+ ions $[\Delta G^o_{t(H^+)}]$ in different mixed solvents have been determined. The equilibrium constants for the reactions

$$\text{Febipy}_3^{2+} + 3\,H^+ \rightleftharpoons Fe^{2+} + 3\ \text{bipy}\ H^+$$

$$\text{and Febipy}_3^{2+} \rightleftharpoons Fe^{2+} + 3\ \text{bipy}$$

in dmso + H_2O and formamide + water have also been determined.

The chapter II of the present dessertation consists of a brief discussion on the different aspects of kinetics and reaction mechanisms of the inorganic reactions and the results of our investigations on the formation and dissociation reactions of ferrodiin and ferroin in different dmf + water mixtures (0 - 100% dmf).

The last chapter begins with a brief introduction of spectral behaviour of compounds in different solvents particularly emphasizing spectral solvent shifts.

Studies on the spectral aspects of the (1,10-phenanthroline and 2,2'-bipyridine) particularly the spectral solvent shifts and solvatomatochromic behaviour of ferrodiin and ferroin have been incorporated in sections II and III of chapter III. The results indicate that both solute and solvent are responsible for spectral solvent shifts and for solutes with hydrogen-bonding capability, blue shift is observed in going from non-polar to polar solvents be it $n \longrightarrow \pi^*$ or $\pi \longrightarrow \pi^*$ transitions.

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