

C H A P T E R - I

INTRODUCTION :1.1 Solutions in water :

If one establishes a hierarchy of importance among solvents, water must certainly be appropriated a prime position among solvents because of its major role in natural biological processes. It is a necessary condition for life. Life began in oceans of earth and evolved there. Water determines not only the structural configuration, but the biological function of biomacromolecules. The living tissue contains around 70% water is by now well worn cliché. To what extent and in what manner water is necessary to the operation of a biological system is, however, still uncertain. The peculiarities of water have been utilised by and incorporated into the fabric and working of the life processes in the most delicate way. Water is the most common solvent for all of chemistry. The physical nature of liquid water, its role in life processes and its occurrence and distribution presents a wide spectrum of problems to physical, life scientists and engineers. Better understanding of solute-water interactions at molecular level can help in solving many life science problems like enzyme catalysis, biological mass transport and formation of biological structures from

molecules and molecular aggregation.

Liquid water, the most extra-ordinary substance, is anomalous in everyone of its physical and chemical properties as compared to other organic and inorganic liquids. The majorities of these anomalies reflect some of the water properties, namely the ability of water molecules to interact specifically to the molecules of other substances. The tendency of water molecules to stick together is nicely illustrated by the large amount of energy required to melt and evaporate the substance and the high temperature at which these molecular separation process occur. The anomalously high transition temperatures of water clearly indicate that the water molecules are loath to separate from one another. Clearly some force is holding them together and prevent their escape.

The structure of water is the most difficult to decipher, as it has too high an enthalpy and entropy of vaporisation. The liquid is denser than the solid and shows a maximum density at 4°C , so that between 0°C to 4°C the density increases with temperature. Its heat capacity is also abnormally large. The molecule of water is so small but its surface tension is high.¹

In order to understand the anomalous behaviour, the structural interactions and their implications,

one should proceed to review first the problem of structure of water and then the aspect of solute-solvent and solute-solute interactions in aqueous solutions.

A number of models were proposed which involved extensive structuring different from that of ice. L. Pauling suggested cages of hydrogen bonded water molecules with an additional in the centre (Fig.1).² Frank H.S. and Wen suggested that hydrogen bonding might be somewhat cooperative, that is, the formation of a second and a third hydrogen bond should be easier, based on dipole moment consideration than that of the first bond.³ The effect would be that once a few molecules had hydrogen-bonded a rather large cluster would grow easily (Fig.2). A later fluctuation would cause the cluster break up. The idea is one of "flickering cluster". Dielectric studies on water show that molecules are able to respond to an alternating electric field up to very high frequencies, about 10^{10} sec⁻¹. This means that any structured region must be very short-lived about 10^{-10} sec or about 10^3 vibrations, hence the term "flickering clusters". Judging from the characterising energy for the change in fluidity with temperature and similar energy values obtained from dielectric relaxation and sound absorption.⁴

The "flickering cluster" theory was further

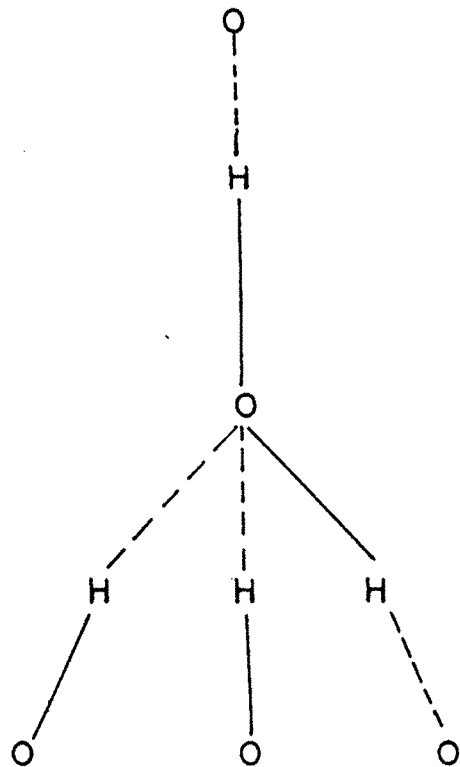


Fig.1. Hydrogen bonded water molecule

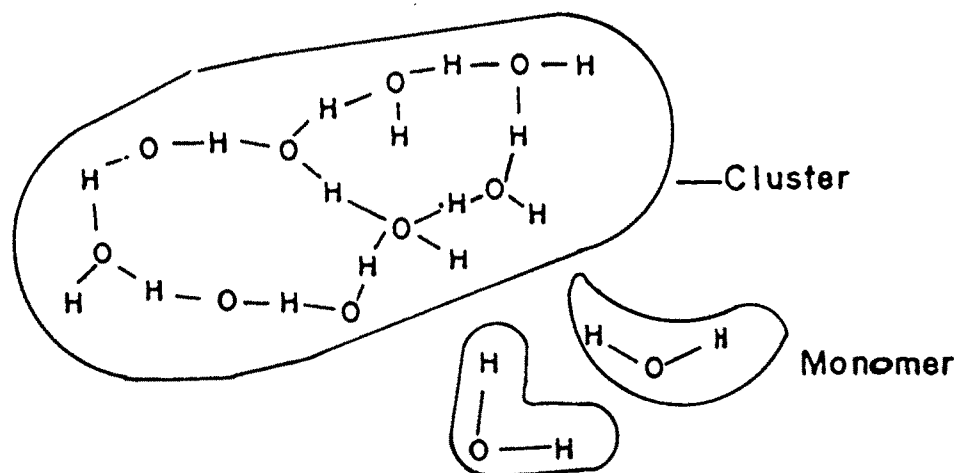


Fig. 2. Frank-wen flickering structure of liquid water

developed in a quantitative manner by Nemethy and Scheraga.⁵ This model visualises liquid water as consisting of a mixture of hydrogen bonded polymers or clusters and more or less free or monomeric water. At room temperature an average cluster contains about 40 water molecules. Small polymers tend to be rare because of the cooperative nature of the hydrogen-bonding process.

One of the most interesting features of the structure of water, however, is the angular correlation between molecules, as determined by the pattern of hydrogen bonds. The X-ray diffraction can not provide this information. Neutron diffraction and electron diffraction studies can, however, yield pertinent data. It is necessary to use heavy water, D_2O , because neutron scattering from proton is mainly incoherent owing to nuclear spin effects. The neutron-diffraction results indicate that water has a less ordered structure than previously believed.⁶

It is generally recognised that structure phenomena in aqueous solutions are associated with large heat capacity changes, and hence the extreme temperature sensitivity of many of the thermodynamic properties of solutes in aqueous solutions points to the importance of solute-water interactions in such system. The term structure

as applied to a liquid, must be placed in its right context. In liquid water the molecular reorientational time, resulting either from rotational or translational diffusion, is of the order of 10^{-11} sec and if a dissolved solute can markedly lengthen this period, say 10^{-10} sec, the effect can be referred to as structure promotion.

The study of the structure of water and of aqueous solutions has recently received far more attention in commercial desalination of sea water and developments in molecular biology.⁷ In the past few decades a study of the role of water in the neighbourhood of solute particles has been the preoccupation of a large number of experimentalists and theorists engaged in liquid-phase solution chemistry. Many lines of enquiry have focused on the phenomena associated with solvation in water and the interpretation in terms of structural changes in the solvent about solute particles. The study of aqueous solutions reveals important contributions to the properties brought about by changes in hydrogen bonding in the solvent in the proximity of dissolved solute particles.

In the recent years more and more investigators have devoted their efforts to the study of the thermodynamics of solute-solute interactions and solute-solvent

interactions. The main objective of these studies has been to gain insight into the phenomenon of hydrophobic interaction which plays an important role in many biochemical processes. The term hydrophobic interaction is commonly used to indicate that the association of solute molecules through their apolar moieties with the favourable influence of water as a solvent.⁸

Most important and widely accepted model for aqueous electrolytic solutions is due to Frank and Wen (Fig.3). According to them, there are three distinct regions. At a sufficient distance away from the ion, the influence of charge (ion) is negligible and therefore, normal structure of water is retained i.e. similar to bulk water. In a region between water sheath and bulk water two forces are operating, one due to an ion and second due to bulk water, the former tries to align the water dipoles parallel to the spherically symmetrical ionic field, and the water in between region continue to have the tetrahedral arrangement. In this region (in-between) water adopts, a compromise structure between two type of influences. In this intermediate region, the water structure is partly broken down or partly more hydrogen bounded which depends upon the valence, radius and nature of the ions under consideration.

Character of an ion as a water structure maker

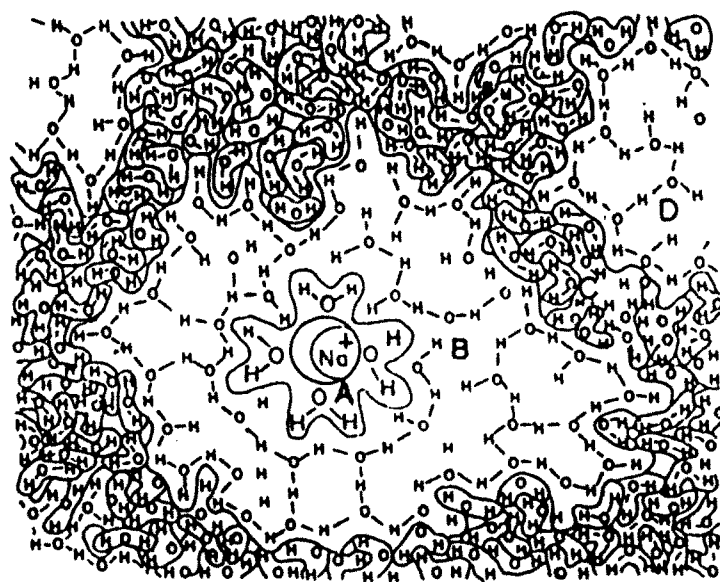


Fig.3. The local water structure near a cation in aqueous solution : A, innermost, dense, lightly bound electrostricted region ; B, Frank-Wen cluster-like region ; C, broken water structure region. D, bulk water.

or structure breaker is determined by the relative importance of region A, B and C. We know much less about the hydration of anions than cations, but it is generally said that common anionic (like Cl^- , Br^- , NO_3^-) are structure breakers. Generally it is found that small ions and multivalent ions such as Li^+ , H_3O^+ , OH^- and F^- increase the viscosity of water, presumably by increasing the amount of structures, thus they are said to be structure makers⁹. Their high electric fields not only polarise, immobilise and electrostrict neighbouring water molecules, but they include additional order (entropy loss) beyond the first water layer (i.e. secondary hydration) according to Bockris encroaching on the structure broken region. According to Samoilov, the activation energy for the exchange of neighbour water molecules about each ion is positive i.e. the primary hydration water is less mobile than bulk water (positive hydration)¹⁰. It is also found that large monovalent ions have a net structure breaking effect. Thus, ions such as K^+ , Rb^+ , Cl^- , Br^- , I^- actually increase the fluidity of water, that is decrease the viscosity.

Viscosity is the most general and important method used for evaluating the structure making behaviour of dissolved electrolytes and decreases due to structure breaking behaviour of dissolved electrolytes. The dependence

of viscosities of solutions on electrolytes concentration can be represented by the Jones Doles equation.¹¹

$$\eta = \eta_0 (1 + A\sqrt{C} + B.C + \dots) \quad \text{----- (1)}$$

Where, η and η_0 are viscosities of solution and solvent respectively. Most of the viscosity studies are aimed at the determination of B-coefficients because viscosity B-coefficient is an useful parameter for the study of ion-solvent interactions and measures the order or disorder introduced by the ions into the solvent structure i.e. the modification of solvent structure in the immediate vicinity of ions.

Second most important experimental method is conductivity measurements. It is found that ordered water structure influence mobility of the ions and hence conductivity. The effect of pressure and temperature on the 'walden product' also gives information about the structure breaking or structure ordering by the ions.¹²

Density, sound velocity and compressibility properties also give indirect information about the structural interaction in solution. The apparent molal volumes and compressibilities can be calculated from these properties in solution. These methods are now a days more popular

because accurate data of sound velocity and density could be obtained upto very low concentration of electrolytes in water.^{13,14}

The derived properties like apparent molal volumes (ϕ_v), apparent molal compressibility (ϕ_k) and apparent molal heat capacity (ϕ_{cp}) of salts have proved to be of great value in the understanding of ionic interactions.

Masson have shown that the apparent molal volume (ϕ_v) of a number of ionic solutes varies linearly with the square root of the concentration \sqrt{C} . In dilute solutions and often in concentrated solution also.¹⁵ Thus,

$$\phi_v = \phi_v^0 + S_v \sqrt{C} + B_v m \quad \text{----- (2)}$$

Where ϕ_v^0 is apparent molal volume of infinite dilution and S_v is the experimental slope. In the same way adiabatic compressibility ϕ_k can be equal to

$$\phi_k = \phi_k^0 + S_k \sqrt{C} + B_k m \quad \text{----- (3)}$$

Where ϕ_k^0 is apparent molal compressibility at infinite dilution. The values of S_k and S_v can be obtained from Debye-Huckel theory. These slopes are specific for different electrolytes.¹⁶

It has been explained that negative limiting

partial molal compressibilities are due to structure breaking effect of electrolytes, as the infinite dilution properties give information about the ion-solvent interaction.¹⁷

The special type of interaction between water and apolar groups provides the most interesting manifestation of the phenomenon called the hydrophobic interactions. The primary contribution to the strength of this interaction comes from changes in structure of water when non-polar groups associate. Hydrophobic interactions play an important role in the specificity of reactions and on the stability of biological systems in water.

Since, hydrogen bonding and electrostatic interactions are also involved in biological systems, most of the information on hydrophobic interactions comes from systematic studies of model compounds. The symmetrical tetraalkylammonium halides ($R_4 NX$) have been widely used as model compounds as they possess both ionic charge as well as hydrophobic residues in the forms of non-polar alkyl groups. Solutions of tetraalkylammonium salts in water show many interesting physical properties.¹⁸

1.2 Mixed aqueous solvent system :

Mixed aqueous media are finding increasing

applications in the fields of electrochemistry, chromatography, solvent extraction, kinetic studies, colloidal science and biochemistry. Water and mixture of water within organic solvents are commonly used as a solvent, since they display remarkable and often amazing solvent effects on the rates and thermodynamic activation parameters of nucleophilic displacement reactions, acid-base catalysed processes, and many other important reactions in organic chemistry. The unique structural properties of water, as a bulky and dense species, play an important role in governing the solution properties of non-electrolytes in water.¹⁹ The structural interactions in aqueous solutions are generally associated with large heat capacity changes and changes in volume, enthalpy and entropy.

The physical and thermodynamic properties of aqueous binaries strongly depend on the nature of the non-aqueous component. Deviation from ideal behaviour is quite a common phenomenon and may lead to eccentric solvent properties. Mixed aqueous binaries offer the possibility of continuously changing the three dimensional hydrogen-bond network of water by gradually increasing the mole fraction of the organic component. If the organic solvent is completely dissolved in water, large changes in solvent properties are observed. In DMF-water, for instance, the dielectric constant

may be varied from 78(H₂O) to 36.7 (DMF) at 25° C.

N,N-dimethylformamide (DMF) as an aprotic solvent is an example of a 'pure' dipolar fluid. Since the hydrogen bond is absent, the liquid structure of the neat DMF is determined by the dipole-dipole interactions between molecules. Addition of water modifies this picture; hydrogen bonds between oxygen atoms of the amide group and water molecules are created. In the literature many papers showing (by using various experimental techniques) that association complexes of the DMF·nH₂O type exist in the DMF + water mixture.²⁰

Mixtures of aliphatic amides and water have been the subject of many studies.²¹ Since these amides cover a very wide range of dielectric constants and are usually miscible with water, they are often used in studies of the interrelations between the solubility of drugs and the dielectric constants of the pure compounds and of their aqueous mixtures. In addition, the amides can serve as model compounds for the investigations of the properties of peptides in aqueous solutions. Among these amides, DMF is of particular interest in view of the lack of hydrogen bonding in the pure solvent. Therefore we had used this solvent and its aqueous mixtures to study the influence of solvent

structure on the solvation of a third component. For example the peculiar properties of hydrophobic solutes can be examined rather systematically, since it is possible to go from pure water to pure DMF, i.e. from a very structured solvent to a solvent where specific structural effects are absent.

It is well known fact that the free energy, enthalpy and entropy of solution is a function of concentration. At a particular concentration they shows a maximum or minimum. Certain properties like partial molal volume and compressibilities of solutions show minimum in low concentration region. A detailed account of these properties has been reviewed by Franks and Ives for aqueous solution of alcohols.²² Generally these extrema are accounted in terms of solute-solute and solute-water hydrogen bonding interactions. Recently, Patil et. al.²³ have shown convincingly that the extremas for different properties in case of alcohol-water systems are due to hydrophobic hydration in dilute region while the others at higher concentrations (x_2 alcohol \approx 0.2 to 0.4) are due to hydrophobic interactions i.e. solute-solute association.

In aqueous dilute alcohol solutions the structural effects are generally accounted in terms of

hydrophobic interactions and solute-solvent interactions. A better way of understanding of these subtle effects in water is to study the compressional effects at various temperature. From this point of view there is a great need of compressibility studies in dilute solutions as these signify the stability imparted by the water molecule layers around the solute molecules against the thermal and pressure effects. But the recent literature survey reveals that there are very few solutes for which such studies have been undertaken.

Kaulgud and Rao studied the apparent molal compressibilities of alcohols through a wide range of temperature ($5^{\circ}\text{C} - 45^{\circ}\text{C}$) in dilute region.²⁴ From their observations they concluded that the values of ϕ_k° are negative at low temperature and becomes more negative as the the chain increases (except for methanol where ϕ_k° is positive). At higher temperature the values of ϕ_k° are positive for all alcohols. ϕ_k° values at lower temperature become less negative as the molecules becomes more compact. The small and positive ϕ_k° values for methanol indicates that the MeOH molecules at all temperature go into solution without much affecting the free water molecules. The values of ϕ_k° for t-Butanol are less negative than n-Butanol. This is explained on the basis of symmetry, wherein t-BuOH is accomodated

easily in the natural cavities in the water without disturbing much the free water molecules. The negative and positive slopes of $\phi_k(X_2)$ curves suggest occupation of cavities and solute-solute interactions respectively.

Kaulgud and Patil²⁵ have suggested that ϕ_k^0 value represent better criteria for the structure breaking and making properties of the solute. The concentration variation of ϕ_k gives information about solute-solute interactions. However, the concentration variation of ϕ_k has not been studied in detail except for aqueous amine solutions at 20° C. Recently Desnoyers et al²⁶ and Benson et al²⁷ have confirmed the observations of Patil that ϕ_k for aqueous methanol and ethanol solutions show negative concentration dependence. The negative slope have been interpreted by Kaulgud and Patil in terms of substitutional dissolution of amine molecules in water. They have further explained that interstitial dissolution in cavities made on demand by water molecules by forming more hydrogen bonds and suitable cavities (structure making effect) around the large solute molecules, results in positive slope for ϕ_k paramter.

It is already noted that the abnormal thermodynamic properties of aqueous solutions of non-electrolytes, compared with the properties of non-aqueous

solutions, are related to the increase in the structure of water around non-polar solutes. However, it is recently fully recognised that, the same kind of phenomenon is largely responsible for the peculiar behaviour of tetraalkyl-ammonium halides and long chain organic salts.²⁸

There is convincing evidence that near non-polar molecules or non-polar groups, there is a reinforcement of hydrogen bonds of water, which on a time average may be expected to be of the order of a few molecular diameters thick. The exact nature of this shell of structured water is still uncertain, it may be ice-like, clathrate like or non-tetrahedrally hydrogen bonded. This kind of hydration does not result from strong solute-solvent interactions brought about by hydrophobic group or molecule. It is for this reason that it is termed as hydrophobic hydration.

The theoretical aspects of hydrophobic hydration have recently received ~~for~~ more attention from the work of Kauzman and Coworkers.²⁹ The excess thermodynamical properties have been subjected to Mayer-MacMillon theory by Kauzman extended by Friedman.^{30,31} They have found that the virial coefficients occurring in linear expanding equations of volumes and activity coefficients are related to

solute-solute interactions and support the notion of hydrophobic dissociation in dilute aqueous solutions. Patil following Ben-Naim's approach has shown that for t-butanol-water system, hydrophobic hydration exists in solution but the strength of such interaction decreases with the concentration of alcohol.³²

1.3 Solutions of electrolytes in non-aqueous solvent :

There has been an increasing interest in the behaviour of electrolytes in non-aqueous solvents with a view to investigating ion-ion and ion-solvent interactions under varied conditions. Non-aqueous solvents, in a broad sense may be defined as media other than water which will dissolve a reasonable number of compounds and permit the occurrence of chemical reactions. Generally a non-aqueous solvents are selected such that they are either basic, acidic, amphiprotic, aprotic, protophilic or protogenic.

In the monohydric alcohol, the presence of only one acidic proton per molecule limits structuring to linear chains, whereas polyhydric alcohols, like glycerol and ethylene glycol, are capable of formation of multiple hydrogen bonds but the nature of the intermolecular association in these liquids is still not understood. Although these molecules

are capable of forming multiple hydrogen bonds, a two dimensional sheet like structure occurs in the crystal lattice, and the molecular geometry is not conducive to forming tetrahedral three dimensional network.

The presence of both acidic and basic groups in water and other hydrogen bonding solvents provides effective solvation for both cations and anions. These protic solvents have long been considered a different class from dipolar aprotic solvents which interact effectively with cations through their lone pair but have no sharply definite positive sites for interaction with ions.

Non-hydrogen bonded liquids with high dielectric constant, low acidity, low basicity and good chemical stability are Dimethyl sulphoxide, Acetonitrile, Dimethylacetamide, Dimethylformamide, Nitromethane etc.³³ The thermodynamic data of electrolyte solutions in these solvents are so sparse that one can rarely use them to elucidate ionic hydration.

1.4 Ternary systems :

In a ternary system, the properties of a model compound, are studied in non-aqueous-aqueous binary solvent system, in order to determine the response of the

modified water structure caused by the cosolvent to the presence of the model compound. The recent work on the volumes and compressibility of transfer for electrolytes from water to mixed aqueous solutions are interesting.³⁴ Wazalwar proposed a clathrate type model for aqueous urea solutions, where large alkyl ammonium ions are stabilised as guest molecules through weak hydrophobic interactions.³⁵

The transfer functions involving enthalpies, heat capacities and volumes of ions, from water to several other mixed aqueous solvents have been studied in great details. Kreschek and Benzamin have studied the specific heat of several proteins in water and in aqueous urea using heat capacity data, they have shown that urea acts as structure breaker and competes with water to form ordered structure around the solute.³⁶ Patil, Mehta and Salpekar studied the apparent molal compressibilities of the salts NaCl, Et₄NBr and Bu₄NBr at infinite dilution (ϕ_k^0) from the concentration variation of ϕ_k for these mixtures.³⁷ The transfer compressibilities of these electrolytes ($\Delta\phi_k^0$)_{trans} from water to aqueous tert-butanol solutions show a non linear behavior as a function of cosolvent concentration. From their observations they concluded that structural interaction in binary and ternary systems are similar in nature for NaCl

and Et_4NBr while in the case of Bu_4NBr they are different, probably due to the resultant structure being ice-like and comparatively more rigid.

The infinite dilution properties are found to be helpful in the study of solute-solvent interactions. While the trends at finite concentration, give information about the solute-solute or ion-ion interactions. The hydrophobic hydration play an important role in the specificity of reactions and on the stability of biological systems in water. The properties of aqueous solutions like that of alcohols have been reported largely concerning the problems about volumes, enthalpies, specific heats etc. But a comprehensive work at finite concentrations, for more important thermodynamic parameters like isothermal compressibility, internal pressure and specific heat at constant volumes is lacking.

The spectacular changes in the reactions of ions when transferred from water to various non-aqueous solvents have resulted in much interest in the properties of electrolyte solutions in non-aqueous solvents.

1.5 Present Work :

The literature survey shows that the thermodynamic properties of electrolytes in water and in

mixed aqueous solvent were widely studied, comparatively such data for non-electrolytes in mixed aqueous solvents and electrolytes in non-aqueous solvents are of limited nature.

Hydrophobic hydration plays an important role in the specificity of reactions and on the stability of biological system in water, and hence the knowledge about these interaction is of considerable importance. The fundamental thermodynamic property in a system is nearly always the total property of a system. In the case of dilute solutions, solute-solvent and solute-solute interactions will cause relatively small changes in the total property. Theoretical models are usually derived for the total thermodynamic property and then rearranged to be in the mathematical form as the expression used to represent the experimental data.

Numerous studies have been made of the composition dependence of the physical properties of amide-water systems. A major motivation for such studies is the belief that an enhanced understanding of the structural and energetic consequences of the interactions between amide and water molecules will ultimately lead to a better appreciation of the manner in which water exercises thermodynamic and kinetic control over the chemical activities of polypeptides in aqueous media.

We have investigated the composition dependence of density and sound velocity properties for DMF-H₂O system at 25^o C across the entire range of mole fractions. The data was used to calculate molar volume and adiabatic compressibility properties. Further, the thermodynamic properties like apparent molar volume (ϕ_v) and compressibility (ϕ_k) of DMF were calculated. The infinite dilution properties (ϕ_v^o and ϕ_k^o respectively) of DMF and their variation with concentration of DMF are examined to understand solute-solvent and solute-solute interactions in solution phase.

It is known that tetrabutyl-ammonium bromide has sufficient solubility in DMF. Therefore, sound velocity and density measurements were carried out for binary system Bu₄NBr and DMF at 25^o C. The infinite dilution properties and their variation with concentration are compared with the properties exhibited by Bu₄NBr in water at 25^o C. The same data was used to obtain transfer functions for volumes and compressibility of Bu₄NBr when it is transferred from water to DMF.

It is wellknown that standard transfer thermodynamic quantities, such as Gibbs free energy (ΔG^o)_t, enthalpy (ΔH^o)_t, entropy (ΔS^o)_t etc. of any solute (i),

which stands for the changes of those quantities accompanying the transfer of one mole of the solute (i) from the standard state in the reference solvent (R) to the standard state in the solvent (S) concerned, i.e. $i(R) - i(S)$, is given by $P_t^0(i) = P_S^0(i) - P_R^0(i)$, where $P = G, H, S$ etc. consequently these quantities are intimately related with the solvent effect in the physico-chemical properties in general and kinetics and equilibria of reactions in particular.

However, the transfer free energy or entropy of solutes from one solvent to other require specification of a standard state. This problem does not arise in case of volumes and compressibility of transfer of the solute. One can indirectly obtain information about structural interactions from these parameters. Therefore, understanding solvent effect on the physico-chemical properties like volumes and compressibilities of the salts we have studied the salts NaCl, KCl, Bu_4NBr salts in water with specific amount of cosolvent i.e. DMF added at $25^{\circ}C$. The appropriate equations are used to obtain infinite dilution properties i.e. limiting apparent molar volumes and compressibilities of the salts. This enabled to calculate the transfer quantities and their variation with concentration of cosolvent (i.e. DMF). The results are explained on the basis of the properties of mixed solvent system, ion-solvent and ion-ion interactions. All these are presented in the following pages.