

CHAPTER - IV

DISCUSSION :

The examination of Figure 11 reveals that density of the ^asolutions does not vary linearly with mole fraction (X_2) of DMF. In general, the density varies linearly with X_2 in case of mono-functional non-electrolytes such as alcohols or amines in water, while it goes through a maximum in case of diols or solutes having more than one polar group. In the present case, it shows a feeble minimum at a concentration of about 0.05 X_2 and then it increases slightly and thereafter decreases monotonously with increase in X_2 to the pure liquid value. Our density value of pure DMF agrees very well with the literature value of 0.9438.⁴² The initial minimum probably can be explained in terms of dimerization of DMF. Such an observation is reported for ~~the~~ first time in aqueous solutions although similar situations exist in case of alcohol- CCl_4 solutions.⁴³ The slight variation in the range of 0.1 to 0.3 X_2 DMF signifies that the polar solute-solvent interactions are not of considerable extent.

The variation of molar volume of $\text{DMF-H}_2\text{O}$ solutions with weight percentage of DMF (Fig.10) shows that

there is a considerable contraction in volume which is maximum at about 0.5 to 0.6 W_2 of DMF. Thus in this system, we observe a negative deviation from linearity of the volume curve.

The sound velocity and isoentropic compressibility parameters go through a maximum and a minimum at a concentration of 0.2 X_2 of DMF respectively (Fig.12). The apparent molal volume of DMF (ϕ_v) goes through a minimum at about 0.15 X_2 , while ϕ_k increases with X_2 (Fig.13). The negative slope of the curve clearly points out that below 0.2 X_2 , DMF-DMF (solute-solute) interactions are prominent and may cause a structure making effect in water. However, such structures are fragile and get disrupted by application of pressure as evidenced from ϕ_k behaviour. The infinite dilution value of ϕ_k (i.e. ϕ_k^0) is $4.5 \times 10^4 \text{ bar}^{-1} \text{ cm}^3 \text{ mol}^{-1}$, which is similar to that of alcohols or amines in water.^{44,45} The limiting excess volume can be obtained from ϕ_v^0 value ($74.6 \text{ cm}^3 \text{ mol}^{-1}$) and pure liquid molar volume (77.38) which comes out to be, $-2.78 \text{ cm}^3 \text{ mol}^{-1}$. This is in agreement with the observations for organic solutes in water.

The results of binary systems NaCl + H₂O, KCl + H₂O and Bu₄NBr + H₂O, (Figs. 8,9) are in agreement

with literature data.^{16,46} The sound velocity and density parameters increase with concentration while compressibility decreases with concentration of the electrolytes. The calculated ϕ_v^0 values (Table VIII) for NaCl, KCl and Bu_4NBr are in fair agreement with the best literature values. The B_v parameter is ^{slightly -ve} positive for structure breaking salts NaCl and KCl, while for structure making salt Bu_4NBr , it is negative. It is ~~has been~~ proposed that in solutions of Bu_4NBr in water, a clathrate like equilibria exist wherein the Bu_4N^+ molecules get lost in the cages formed by water molecules. This phenomena is known as hydrophobic hydration. The negative ϕ_k^0 values for NaCl and KCl signify that Na^+ and K^+ ions are electrostatically hydrated and there is a loss of compressibility of water molecules around the ions. The small negative value of ϕ_k^0 ($-22 \times 10^4 \text{ bar}^{-1}$) in case of Bu_4NBr again points out the subtle structural differences in the solution. The structure of solvent around Bu_4N^+ ions is less compressible. With increase in concentration, ϕ_k increases meaning that the structural entities are more fragile against pressure.

We have studied Bu_4NBr in pure DMF at 25°C . The sound velocity increases with concentration, however the rise in velocity is comparatively smaller than in case of $\text{Bu}_4\text{NBr}-\text{H}_2\text{O}$ system (Fig. 17 and 18). Similarly the β ad

decreases with concentration of Bu_4NBr . The dielectric constant of DMF is ≈ 37 . Hence, the ionization of Bu_4NBr will be less than that of water solutions. On this basis we expect more solute-solute interactions in such solutions. This is evidenced in ϕ_v vs m and ϕ_k vs m curves (Fig.22 a), where one can find that ϕ_v vs m curve shows positive slope while the same is negative in case of H_2O solutions. The ϕ_k rises very steeply suggesting that solute-solute interactions are predominant.

The limiting apparent molar volume (ϕ_v^0) and limiting apparent compressibility (ϕ_k^0) of Bu_4NBr in DMF are $294.4 \text{ cm}^3 \text{ mol}^{-1}$ and $-10 \times 10^4 \text{ cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$ respectively. The ϕ_v^0 value is distinctly smaller than the same in H_2O solutions, while the ϕ_k^0 is of comparable magnitude to that of H_2O solutions. The limiting properties are measure of solute-solvent interactions. Probably there are not much different in these two solvent systems involving Bu_4NBr .

The sound velocity increases with concentration of NaCl in mixed DMF- H_2O solvent system. However at 0.32 X_2 DMF the rise in velocity is comparatively smaller than that of lower DMF-mole fractions (Fig. 14,15). Similar observations can be made for KCl in DMF + H_2O solvent system (Fig. 16). In case of Bu_4NBr in DMF- H_2O system

the velocity increases in lower mole fraction region as well as at higher mole fraction region of DMF-H₂O solvent system. The rise is comparatively smaller at 0.5 and 0.7 X₂ of DMF-H₂O system. In case of 0.3 X₂ of DMF the velocity goes through a small maximum and decreases with further in concentration of Bu₄NBr. Exactly opposite behaviour is observed for the compressibility parameter for these salts in DMF-H₂O solvent system. These observations point out that in 0.2 to 0.4 X₂ DMF in H₂O region the DMF-H₂O interactions dominate the behaviour of sound velocity and compressibility properties of salt-DMF-H₂O systems. The dielectric constant generally varies linearly in such mixed-solvent systems and hence it may not be the only cause for such observations.

The apparent molar volume ϕ_v of NaCl in general increases with concentration for various DMF-H₂O solvent systems (Fig. 23). The variation of ϕ_v parameter can be represented as

$$\phi_v = \phi_v^0 + B'_v \cdot \sqrt{aq.m} \quad \text{----- (19)}$$

Similarly, the apparent molar compressibility of NaCl increases with square root of aquamolality of NaCl at various DMF-H₂O solvent systems. Its variation can be expressed as

$$\phi_k = \phi_k^0 + B'_k \cdot \sqrt{aq.m} \quad \text{----- (20)}$$

We have collected the ϕ_v^0 , ϕ_k^0 , B'_v and B'_k parameters for NaCl, KCl and Bu_4NBr at various mole-fractions of DMF in H_2O in Table X.

Our B'_v and B'_k are not enough reliable because of the non-availability of exact Debye-Huckel limiting law information for such mixed aqueous solvent systems. However, their tentative magnitudes and sign can furnish important information about ion-ion interactions.

In general, the interactions of Na^+ ions with water are interpreted as a slight structure making action of surrounding water molecules while the interactions of K^+ ions with water are attributed to structure breaking action in solution. In solutions involving KCl and DMF- H_2O , we can observe this peculiar phenomena very prominently. One can note from the table X, that in case of NaCl, the B'_v parameter is positive for all the mole fractions of DMF in H_2O . While B'_v becomes negative in case of KCl at 0.15 and 0.22 mole fractions of DMF in H_2O . We can interpret this, that the DMF- H_2O complexes which occur with contraction in volume can interact with Na^+ ions and K^+ ions differently. In latter case the ion-ion interaction are similar to that hydrophobic hydration causing B'_v parameter to become negative.

The variation of ϕ_v parameter in $\text{Bu}_4\text{NBr-DMF-H}_2\text{O}$ system is also very much interesting (Fig. 25, 26).

The B'_v parameter (Table Xc) for this system is initially negative meaning that at small concentration of DMF in H_2O , the interactions are similar to that of aqueous binary electrolytic system. At 0.055 X_2 of DMF, the B'_v is almost zero, which again increase with increase in DMF concentration, while at very high DMF concentration it becomes negative. These observations clearly point out that DMF- H_2O solvent system exhibit three region of concentrations, where different types of interaction determines the solution properties. Similar conclusion can be drawn from ϕ_v^0 parameter (measure of ion-solvent interactions) for the salts in these mixed solutions to be discussed latter.

The ϕ_k 's of NaCl, KCl and Bu_4NBr vary linearly with square root of aquamolality of salt at all mole fractions of DMF in H_2O . This signifies that the structures formed are labile against pressure (Fig. 27 to 31). The limiting ϕ_k values (i.e. ϕ_k^0) are collected in Table X for various mole fractions of DMF in H_2O alongwith B'_k parameters.

The transfer functions for volumes and compressibilities for electrolytes (i.e. $\Delta\phi_v^0$ and $\Delta\phi_k^0$ respectively) which are defined by :

$$\Delta\phi_v^0 = \phi_v^0(\text{DMF} + \text{H}_2\text{O}) - \phi_v^0(\text{H}_2\text{O})$$

and

$$\Delta\phi_k^0 = \phi_k^0(\text{DMF} + \text{H}_2\text{O}) - \phi_k^0(\text{H}_2\text{O})$$

are plotted as a function of the mole fraction of DMF in figures 32 and 33 respectively. Both the transfer functions show a strong dependence on the DMF concentration and dependence varies with the nature of electrolyte. Fairly sharp changes are observed in the region where ϕ_v of DMF goes through a minimum. A second transition area in the ternary system is seen at about 0.5 X_2 of DMF where contraction in volume is maximum or viscosity and heat capacity^{47,48} go through a maximum in binary DMF-H₂O system in case of ~~Bu₄NBr + DMF + H₂O~~ system.

These results cannot be interpreted in terms of charge-dipole interactions or in terms of specific interactions involving C=O group since similar trends (although less pronounced) are also observed with other mixed solvents such as t-BuOH-water system.¹⁴ If DMF promotes the structure of water at least at low concentrations (through hydrophobic hydration), then we can attempt to account for the transfer functions in terms of the passage of electrolyte from a structured medium (i.e. H₂O) to a more structured medium (i.e. H₂O + DMF).

A better approach to the interpretation of the transfer functions is probably through solute-solute interactions. The electrolyte-electrolyte interactions have to be ignored since we are considering infinite dilution. But it seems that electrolyte-nonelectrolyte interactions are significant. The transfer function $\Delta \phi_v^0$ of Bu_4NBr is qualitatively very similar to ϕ_v of DMF in water. Therefore whatever is their origin, the overall interactions $\text{Bu}_4\text{NBr-D}_2\text{O}$ seems to be similar to DMF-DMF ones. These interactions are of comparatively smaller extent in case of NaCl and KCl solutions.

In the intermediate region, the transfer volume of Bu_4NBr indicate that Bu_4N^+ are associated with DMF aggregates in a way similar to the solubilization phenomena with surfactants. This is also in harmony with the interpretation given by Patil et al²³ to account interactions in alcohol-water systems in the intermediate region. It seems that in case of NaCl and KCl a levelling effect occurs in this intermediate region, while in case of Bu_4NBr , $\Delta \phi_v^0$ goes through a maximum.

It is well known that critical micelle concentration is lowered in presence of alkali halides⁴⁹ and the lowering is usually attributed to a shift in the monomers

micelle by salting-out process of monomers, the ions lowers the solubility of the hydrophobic monomers and by doing so favour micelle (or a microheterogeneity) formation. A similar phenomena may occur in NaCl-DMF-H₂O and KCl-DMF-H₂O system. This can be strongly supported that these salt have a very limited solubility above 0.3 X₂ of DMF.

The $\Delta\phi_k^0$ values at different DMF concentrations show that in case of Bu₄NBr, they are positive and go through a maximum at about 0.3 to 0.4 X₂ of DMF. They +ve ϕ_k 's are typical of non-electrolytes such as alcohols, ethers and amines. The observed behaviour supports our hypothesis of non-electrolyte-solvent interaction more strongly.

The $\Delta\phi_k^0$ values are difficult to interpret in case of NaCl and KCl solutions. There is a one point of doubtful validity at very low X₂ of DMF. If it is assumed to be reliable, then one can see that in very dilute region a slight structure making salt NaCl exhibits a pronounced structure breaking effect upon the more structured solvent (DMF + H₂O), since negative ϕ_k generally means loss of compressibility of solvent and attachment of the solvent to the cation or a molecule. The structure breaking salt KCl exhibit a normal behaviour as a function of X₂ of DMF indicating the rupture of solvent by the application of pressure.