CHAPTER 1

INTRODUCTION

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Jones and co-workers (1907) studied the molecular conductivity and fluidity (reciprocal of viscosity) of many electrolytes such as potassium iodide, ammonium bromide, lithium nitrate, hydrochloric acid, silver nitrate etc. in solvents such as methanol, ethanol, acetone, water at 0 and 25°c. For most of the salts, they observed a minimum in the molecular conductivity in the case of ethanol water mixtures. The minimum in molecular conductivity was also found in the caseof mixtures of acetone with water. This minimum in conductivity was found to be more pronounced at lower temperature and has been shown to be intimately connected with the minimum in fluidity of the mixtures. They believed that the observed minimum was primarily due to change in dimension of the atmosphere about the ions.

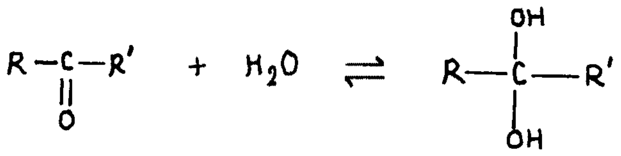
Structure of liquid alcohols:

As the oxygen atom of an alcohol molecule carries one proton and two pairs of electrons, it might be expected to form three hydrogen bonds with its neighbours. This could not be the case for every molecule of an assembly, but it is not obvious why there should not be a distribution of molecules forming one, two or three bonds? All the evidences show that not more than two bonds are formed, each oxygen atom acting once as proton donor and once as proton acceptor. This apparent limitation to equality of give and take may be attributed to the essentially co-operative nature of hydrogen bonding together with the unfavourable steric effect of the organic group, it resticts the degree of order which can preclude a kind of three dimensional association which is dominant in water.

This is evidence that methanol < ethanol < propanol is the order of increasing proton accepting facility.

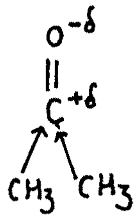
Structure of acetone:

When ketones and aldehydes are dissolved in water they establish equilibrium with their hydrates, gem diols. The equilibrium is not of much chemical interest but it does furnish an indication of the case with which additions can occur across various carbonyl groups.



$$R-\underset{\underset{O}{\|}}{C}-R' + H_2O \rightleftharpoons R-\overset{OH}{\underset{OH}{C}}-R'$$

Formaldehyde is almost completely hydrated, with successive addition of methyl groups one arrives at acetone, negligibly hydrated. This trend is the result of the stabilizing effect of methyl groups on double bonds. In this case the electron feeding methyl groups stabilize the C = O dipole.



Hydrogen bonding in water:

The hydrogen atom can be bound to two atoms instead of one under certain conditions. One of these bonds is covalent in character while the second considerably weaker is called hydrogen bond. The hydrogen bond is believed to be ionic in character and to arise from electro negative attraction between the electrons on the co-ordinating atom and the small positive nucleus of the hydrogen. The hydrogen bond whose strength ranges from 2 to 10 K cal. per mole invariably involves strongly electronegative atoms such as nitrogen or oxygen. Examples of hydrogen bonding are found in water, alcohols, ketones etc. The hydrogen bond between water molecules is formed between the hydrogen of one molecule and the lone pair electrons of another molecule. Thus each water molecule can participate in four hydrogen bonds, two as donor and two as acceptor, in an almost tetrahedral arrangement.

Structure of water:

Modern views on the water structure and structure of ionic solutions are based on the classical studies by Bernel and Fowler (1933). According to the older views the associated nature of water was attributed to the various polymerised forms such as $(H_2O)_2$ and $(H_2O)_3$. But according to Bernel and Fowler the water molecule is pictured as an oxygen ion with two protons embedded in its electronic cloud. On the opposite side of the molecule are centered two negative regions such that all the four fractional charges namely two positive and two negative are directed towards the four corners of a tetrahedron.

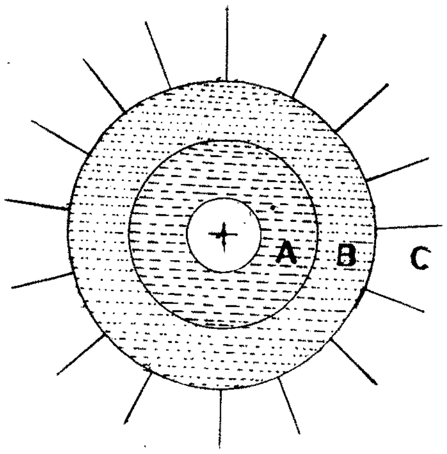
In ice each molecule has four neighbours arranged tetrahedrally and the ice lattice is held together by electro static binding between opposite charges (hydrogen bond). However, when ice is melted there is a considerable contraction indicating that in water the open ordered arrangement gets broken to some extent. In spite of this fact x-ray, infrared and Raman spectra studies of water structure by Magnet (1937) support the tetrahedral co-ordinated structure which accounts satisfactorily for associated nature of water is believed to be maintained by hydrogen bonds and it results from the specially favourable charge distribution and geometry of water molecule. Frank and Evans (1945) from entropy data conclude that the water structure becomes more ordered through the influence of dissolved non polar molecule. However, in aqueous electrolytes an intense electric field (due to ionic charge) is super imposed on the normal interactions between solvent and solute and resultant effect of the ionic charges is to reduce the entropy loss, i.e. to promote increased disorder in the water structure. This effect of disorder in water structure has been found in spite of the fact that in the immediate vicinity of ion, there exists a layer of rather firmly oriented water molecules, depending upon the polarising power of the ion. Depending upon the charge and size of the ion, the ion will orient the water dipoles.

The observation that lithium ion has the lowest mobility of the alkali metal ions. (the others increasing with the increasing radius of cation) was the striking evidence for the existence of the long known phenomenon "hydration of ions".

A critical review of different methods used for finding out the hydration, merits and demerits of each and every method and the comparison of hydration numbers found by different methods is given by Bockris (1949).

According to him a certain number of solvent molecules is firmly attached to the ion and that a further ion dipole interaction takes place involving solvent molecules outside the inner ion-solvent entity. He has defined "primary solvation" as solvent molecules attached to the ions in the solution for which 1) The ion and its attached solvent molecules move together as one entity, during the electrolytic transport 2) The solvent molecules have completely lost their own separate translational degree of freedom. According to him "secondary solvation" may be called as the term referring to all electrostatic interactions which are not included in the definition given for primary solvation.

Frank and Wen (1957) from entropy study have proposed a model for hydration of ion. According to them the idea of "ice-likeness" (ice-berg) in small regions of aqueous solutions is made more precise by the notation of a "flickering cluster" of hydrogen bonded water molecules. As ion in solution is surrounded by three different regions of water molecules.



1) The region A is one of immobilization because of direct influence of electrostatic attraction. (2) The region B is structure breaking (3) The region C contains normal water polarised in the ordinary way by the ionic field.

The magnitude of these regions are dependent on the ionic size and its charge.Several additional sets of data such as heat capacity, dielectric relaxation, ionic mobility and its temperature coefficient etc. support the above mentioned picture. According to above authors the region A which always existed, was composed of the nearest neighbouring water molecules and that an ion, smaller or multiple charged or both (Li^{+} ,F^{-} ,Mg^{++}) might include additional structure (Entropy loss) of some sort beyond the first water layer. Such encroachment on region B might extingwish the region B and would result in structure making. Larger singly charged ions (I^{-},Cs^{+}) seem to have a large structure breaking effect where in the region B encroaches on region A.

A similar picture as proposed by Frank and Wen has been reached by Samoilov (1957). He has worked out a method for calculating, from self diffusion measurements, the average time that a water molecule spends in the immediate vicinity of ion. According to him if the exchange of water molecules in the immediate vicinity of the ions is considerable and as the frequency of the exchange grows the hydration of the ions weakens. He has further pointed out that the exchange in activation energy (because of ionic influence) of the exchange of water molecules in the immediate vicinity (δE) determines the hydration of ions. He concluded that the smaller the ions e.g. Li^+, Na^+ have positive values of δE where as larger ions such as K^+, Cl^- have values of $\delta E < 0$. For ions having negative values of δE, the water molecules near the ion are more mobile than in pure water.

It may be concluded that according to recent views of the ion-water interactions, the solvent water comprises of four regions 1) The water molecules in the immediate vicinity of an ion are strongly oriented and may have lost all rotational freedom. (2) A further shell of the water molecules under the influence of the ionic charge is likely to be partly oriented. After the second layer the influence of the ionic charge decreases. However, in dilute solutions two or three more regions can be distingwished. Those molecules which are most remote from the central ion will maintain the normal tetrahedral structure and the intermediate shells will be accommodating themselves in the different configurations between which they are sandwiched. The clear cut separation between two consecutive shells will naturally be dependent on the size, charge and nature of the ion under consideration.

<u>Properties of mixed aqueous solvents</u>:

The physical properties of alcohol-water mixtures have recently been reviewed by Frank & Ives in some detail.

The interaction betwen water and alcohols are rather more complex than is suggested by a simple acid base proton transfer of the kind.

$$H_3O^+ + RO^- = H_2O + ROH = OH^- + ROH_2^+$$

Both alcohols and water are extensively associated by hydrogen bonding but the two types of association are quite dissimiler and mutally incompatible.

For monohydric alcohols in dilute aqueous solution, the abnormal physical property can be attributed in a general way to the bifunctional nature of solute molecules. The hydrophobic hydrocarbon group may be imagined as resisting the pull into solution exerted by the hydrophile hydroxyl group which either as proton donor or acceptor, can form hydrogen bond with the solvent molecules. A second hydroxyl group in the solute molecule (glycols) shifts the balance of competing influence in favour of aqueous behaviour and the anomolies become less marked. Further, hydroxylation eventually removes them altogether. Thus the sugars are ostensibly, among the most normal of solutes in water.

This is evidence that methanol $<$ ethanol $<$ propanol $<$ butanol is the order of increasing proton accepting facility so that the hydrogen bonding between butyl alcohol and water should be energetically favoured, it may however, be subject to the same steric limitation, which restricts the degree of association in pure ethanol.

Infra-red spectroscopy is of limited use in the study of a alcohol-water systems because the very complex interactions covering a wide and continuance range of energies give rise to broad unresolvable absorption bands. The information more recently available from n.m.r. spectroscopy is not extnesive and because some of it is contradictory require critical assessment. This unfortunate situation may be due to the very great sensibility of proton exchange to catalysis by trace impurities, perticularity of acids and bases. Static dielectric constant of ~~[illegible]~~ alcohol-water mixtures does not show very significant effect of structural complexity.

The solubility behaviour is at odd with the acceptable view that alcohol-water mixtures show positive deviation from Raoult's law, where solute exhibits a negative temperature dependance of solubility, the solvent acidity coefficient (γ_1) must be less than unity. Most of the older work on such mixture was based on vapour pressure measurement performed at temperature and concentrations at which $\gamma_1 > 1$. A recent comprehensive study combining measurements of freesing point depression, heat of mixing and heat capacities enabled γ_1 to be calculated for series of dilute mixtures over the temperature range - 10 to 30°c and it was found that for alcohol-water mxitures log γ_1 is negative at low temperatures. By applying a modification of the Gibbs-Duhem equation the solute activity with Henry's law as standard states can be evaluated and it is seen that at low temperatures and concentrations, the volatility of the alcohol in the aqueous mixtures becomes higher with increasing concentration than is predicted by Henry's law, but vapour pressure results indicate that the activity isotherm must cross the reference line giving rise to a pseudoideal system.

Turning to the alcohol rich end of composition scale, the excess functions in this region are consistant with the postulate of depolymerisation of alcohol aggregates resulting from the introduction of water. This is perticularly striking in the case of higher alcohols, e.g. tertiary butanol where the mixing process becomes endothermic for alcohol rich solution. Rather similar results are obtained by the addition of non polar diluents, e.g. carbon tetrachloride to alcohols. Indeed by the superposition of acetone-chloroform and methanol-carbon tetrachloride diagram is arrived at a type of behaviours which is characteristic of tertiary butanol-water system. The magnitude of the endotherm effect in aqueous alcohol solutions is some what smaller than in the solutions of alcohol in non polar solvents. Possibly in aqueous mixtures, some of the positive enthalpy of depolymerisation is off-set by an exothermic contribution due to inter component hydrogen bonding. The existence of water central association complexes has been suggested to explain the results of experiments on the diffusion of water in various alcohols.

In the view of the explanation put forward to account for the thermodynamic functions of alcohol-water mixtures it is some what of a puzzle why the excess functions of mixing for the system dioxane-water are almost identical to most of the tertiary butanol-water system at the same temperature. Since dioxane can not be associated in pure state the endothermic mixing in dioxane rich mixtures can not arise from the break down of association complexes by the addition of the other components. Endothermic mixing can also be a feature of systems in which large contribution towards the total interaction arises from dispersion forces, but this too is unlikely in the case of dioxane and water. In some other respect dioxane in its aqueous solutions behave very differently from alcohols in particular water-dioxane mixtures do not show the marked maxima in the sound absorption composition curve which are considered to arise from structural effects.

Small additions of some non electrolyte to water will lead to an increase in long range order, or to an increase in the half life of whatever structural entities do not exist in water. Other non-electrolytes equally capable of hydrogen bonding probably reduce the structural integrity of liquid water, specifically the two types of behaviour are not always easily distinguishable. For instance a maximum in the viscosity concentration curves in the binary system is some times related to structural promotion and both the systems water-ethanol and water-dioxane exhibit such behaviour. However, for ethanol-water system $d\eta/dC$ increases with increasing concentration, showing an increased structural effects which reaches a maximum. In the water dioxane system $d\eta/dC$ decreases with increasing dioxane content. Difference in the two systems also becomes apparent from a study of derivative curve the high concentration region.

In summary, therefore, the experimental evidence indicates that some types of organic non-electrolytes affect water in such a way that an increase in structural order compared to that which exists in pure water is produced.

At the other end of the composition scale a depolymerisation of hydrogen bonded aggregates results from the introduction of water and the solution properties of the mixture must be interpretated in terms of at least three competing effects.

D'Aprano Alessandro and others (1979) have studied the viscosities of water in normal aliphatic alcohols at 15°c, 25°c, 35°c and 45°c. The results showed that water decrease the viscosity of alcohols and there is a formation of water centered complex.

Ion effect :

Warner A.P. Luck (1987) describes the structure of water by using - infra red spectroscopy. He also discussed the effect of ions of the added salts on the mutual solubility of water and non aqueous solvent. The result indicate that "structure breaking" ions increase the solubility of ions in water and non aqueous solvent by a weakening of H-bond structure, while structure makers decrease the solubility of solute in both phases.

Kramer and others (1989) have studied the effect of structure on the water solubilities of alcohols of general formula C_nH_{2n+1} OH. The result indicate that, the influence of structure can be attributed to four direct structural parameters. (Molecular conductivity, number of carbon atoms of the alkyl groups, quality of the α -carbon atom, e.g. normal, iso, secondary, ternary) and degree of branching.

A survey of literature reveals the incompleteness of the work on conductance of electrolyte in mixed solvents. The author was undertaken the study of the conductivity of strong electrolytes in mixed solvents like ethanol-water, methanol-water and acetone-water at various temperatures and concentrations.