CHAPTER 1

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There seems to be an urgent and basic need to explain the reaction, interactions and molecular interactions of the chemicals such as Surfactants, Bio-surfactants, Additives, Dispersants, Stabilizers, Antioxidants, Coagulants, Flocculants (1,2), in aqueous, non-aqueous and mixed solvents (3,4). These studies were supposed to boost up technological industrial, engineering sciences and in the thrust area of current interest. Solvents (Organic, Inorganic and Mixed) were seem to play the key role in monitoring and controlling the solute-solvent and other structural interactions (5,6,7), also certain physico chemical parameters such as heat capacity, transport and static properties of solute in the solution (8,9,10). There are other remarkable studies such as temperature dependent interaction, solvent composition and surfactant phase titrations (11,12,13) where highly pure form of water is made to act as titrant.

Surface – active agents or surfactants owe their name to their interesting behavior at surfaces and interfaces. They are positively adsorbed at interfaces between phases, and the adsorption of surfactant lowers the interfacial tension (I.F.T.) between the phases. Because of their ability to lower interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents and so forth.

All types of surfactants (14) share the property of amphipathy, the molecule is composed of a non-polar hydrophobic portion and a polar hydrophilic portion and is therefore partly hydrophilic and partly hydrophobic. Often the hydrophilic part of the molecule is called the HEAD and hydrophobic part, usually including an elongated alkyl substituent is called TAIL.
The studies of surfactants and inorganic dispersants in their aqueous as well as in presence of certain polymers such as polyvinyl pyrrolidone and polyvinyl alcohols have been reported to be of current interest. The expertise in the field of research have seen a tremendous molecular interactions\textsuperscript{15} and reorientations\textsuperscript{16} in their solutions\textsuperscript{17}, which may be of high significance in the field of Biotechnology, Detergency, Textile Engineering, Pesticides, Insecticides, Food flavors and Additive technologies. Such studies also provide the better understanding of coagulating\textsuperscript{18}, and occulating technique and other important physico chemical\textsuperscript{(19,20)} phenomenon such as Interfacial Surface Tension (I.F.T.) and Interfacial Chemical Potential (I.C.P.). The solubility\textsuperscript{21} effects of these surfactants in their aqueous as well as in the presence of co-solute have been observed by the chemists\textsuperscript{22} in the field of surfactant to explore out a simple and authentic engineering for their important studies of high applicability.

Bio-medically surfactants have been considered for the workers to be a vital tool\textsuperscript{23} for the studies of number of living systems at the cellular level and at the molecular level.

Our intension in the project has been to cover the wide phase interaction aspects of important surfactants in aqueous and aromatic hydrocarbon solutions by employing measurement of contact angles and wetting coefficients.

Experimental technique used in our work is most authentic, précised and time saving device for phase interaction studies.

Boender etal\textsuperscript{24} described that steady wettings in capillary tube and parallel plate geometries are extended to a spontaneously spreading drop in the presence of a surfactant.

Mixture of surfactants often exhibit synergisms in their physico-chemical properties thus allowing particular application, often mixture may exhibit superior behavior as compared to pure surfactant components. Many reports have been published in
recent years dealing with the solutions properties of mixed surfactants containing ionic, non-ionic or mixed ionic micelles\textsuperscript{25}, however there have been a very few studies analyzing the influence of mixed surfactant systems on reaction processes\textsuperscript{26}. The alkaline hydrolysis of hydroxamic acid on mixed surfactant systems has been reported. The work reported here is part of a wider programme aimed at the understanding of the reaction mechanism in micellar solution\textsuperscript{27}. For the last few years we have been studying the influence of cationic, anionic, zwitter ionic and non-ionic micelles in acidic and alkaline hydrolysis of several hydroxamic acid\textsuperscript{28}. Anionic micelles inhibit the reaction and cationic micelles accelerate hydrolysis. The surface tension variation is governed by the surface transport equation for the surfactant concentration involving a connective term whose magnitude depends on the local meniscus inclination.

When surfactants are present, more than one solution may exist, the one obtained depending on the path followed resulting in hysteresis effects\textsuperscript{17}. Surface tension, which modifies a motion and the associated pressure field, also modifies the apparent contact angle in presence of surfactant\textsuperscript{18}. Wetting includes the motion of surface elements towards the contact line accompanied by a change in their area\textsuperscript{29}. Single emulsion film stabilized by Tetra decyl Tri-methyl Ammonium Bromide in Dodecane phase has been investigated thermodynamically\textsuperscript{30}. Advancing contact angles of different liquids on same solid surface fall very close to a smooth curve when plotted as a function of liquid surface-tension\textsuperscript{31}. From this pattern an equation of state was developed to facilitate the determination of Interfacial tension from contact angles\textsuperscript{32}.
1.1 ROLE OF WATER FOR SOLUTE-SOLVENT INTERACTION

The properties of liquid water in relation to its structure in the presence of additives of low molecular weight have been studied. The purpose of this is to substantiate the fundamental role of water on specific features of aqueous two-phase solution systems\textsuperscript{33}. Organic solvents such as alcohols, acetone, acetonitrile etc. are fully miscible with water while the aromatic hydrocarbons (Benzene, Toluene, Xylene) taken in our work are immiscible with water. These physicochemical properties of water could be of use in explaining our results. The phase separation in water-aromatic hydrocarbon can be reduced by the addition of surfactants. The properties of water in the mixtures are of immense importance. Effects of inorganic salts on the properties of water are of great use as these effects have remarkable importance in phase interactions i.e. the properties of phases in aqueous two phase systems with salt additives.

The importance of liquid water is due to the ability of molecules of water to participate in hydrogen bonding (H-Bonding). This ability could be due to specific distribution of electron density in the molecule.

The association of water molecules in the vapour phase was assumed to produce dimers with a linear hydrogen bond (H-bond) as was found by molecular beam microwave spectroscopy\textsuperscript{34}. According to the quantum mechanical calculations for the water dimer, moderate rotations of the water molecules about their oxygen atoms were of small energy cost, provided the donated hydrogen remains essentially on the symmetry axis. Motions that move the donated hydrogen off axis was reported to increase the dimer energy significantly\textsuperscript{35} the calculations also indicate that after forming a first H-bond, the charge distribution within the
molecules pair is altered in such a way that hydrogen acceptor molecule becomes potentially an even better hydrogen donor than before. In other words, the water molecule was found to be capable of forming a stronger second H-bond due to existence of the first H-bond. Similarly, the proton donor acquires an enhanced ability to accept hydrogen due to the H-bond that it has already formed. This particular feature of H-bonding in water could be called “co-operativity” and it might be fundamentally important for the structure of liquid water.

The essential feature of the H-bond responsible for the intermolecular arrangement of water molecules was of the angular dependence for the water structure. Pople was of the view which indicated that “bent” H-bond i.e. the ones nonlinear in the O-H...O direction were associated with an attractive potential energy dependent on the popkie- et.al. for water dimer in vapour phase. In liquid water this dependence could be affected by existence or absence of the second H-bonds presumably formed by the participating molecules. This function was not available as yet but the view that the energy levels of water molecules (or those of H-bonds) in liquid water should be described by an essentially continuous broad distribution, which was consistent with numerous experimental observations made by various scientists in field of water structure research.

The structure of liquid water could be defined if the following four factors were determined: i) the positional correlation between a given molecule and its first, second, third, etc. nearest neighbors, ii) the coordination number, i.e. the mean number of nearest neighbors to a given molecule, iii) the angular correlation between the nearest neighbors, and iv) the number of broken H-bonds and the extent to which the existent H-bonds were bent while still providing a given intermolecular arrangement. It was noted above that while the first two factors determined experimentally by means of the ray and neutron scattering techniques,
1.2 WATER POTENTIAL IN MIXED SOLVENTS

The solvent properties might cover the ability of the solvent molecules to participate in all possible, specific and unspecific intermolecular interactions between the solvent and solute molecules. The possibility to use physical characteristics of a solvent, such as its dielectric constant, dipole moment, refractive index surface tension, it was argued, particularly, that the majority of the physical properties of a solvent represents the intermolecular interactions occurring between the molecules in the pure solvent, but not the ability of the solvent to interact with a solute.

One of the most important properties of a solvent clearly could be of ability to dissolve various solutes. The phenomenon of the relative insolubility of nonpolar compounds in water by hydrophobic effect. Hydrophobic effect should be observed in aqueous solution as well as in pure water but the propensity of the effect depends on the solution composition. In order to quantify the propensity of an aqueous solution to provoke a hydrophobic effect on a solute, the following approach has been proposed\(^{45}\). The difference in the Gibbs free energy, with transferring or repelling out of a given solute from pure water to an aqueous solution or to an organic solvent it could be used as a measure of the so called solvophobic effect. This term was employed by Abraham et al.\(^{16}\) to stress upon that the effect could be measured not only in pure water but in water organic solvent mixtures of various compositions. The solubilities of nonpolar solutes such as argon alkanes upto n-octane, and some cycloalkanes and other alkane like compounds, in pure water and in water organic solvent mixtures were determined, which could provide some breakthrough for the concept of "made solubility".

The solvent properties of the aqueous solution of a given additive were displayed with respect to a solute which meant that we could deal not just with binary "water + additive" system was seen to be much more complicated than the binary one.
The most important and pertinent question in our studies of these systems might open the options whether there could be a direct solute additive interaction. The possibility to provide the answer usually was felt to depend on the particular experimental technique employed.

Numerous physical properties of any component of an aqueous ternary system may be used to monitor and govern the interaction in such a system. If optical, NMR and other spectroscopic, etc., properties of water were to be examined the conclusion usually could be drawn in relation to the water structure in the system. An illustrative example was offered by the data that organic additives, such as dimethyl sulfoxide [DMSO] and 1,4-dioxane or acetonitrile and 1,4-dioxane were seen to affect each other's capability of modifying the structure and/or the energy distribution of the water-water H-bonds when water was subjected for such modifications present in a great excess.

If the physical properties of a solute in an aqueous ternary system were to be monitored and experimented to examine the interactions in the system, the interpretation of the experimental observations could be seen to depend on the answer to the question of preferential salvation of the solute either by water, or by additive, or by both. To illustrate the common difficulties presumably encountered in the studies of ternary aqueous systems those typical for the solvatochromic studies of water organic solvent mixtures may be considered. The addition of initial amount of an additive may result in replacement of non-bonded single water molecules located in the cavities of the H-bond network of water by the additive molecules. The structural equilibrium in water might be shifted increasing the fraction of H-bonded network molecules. At the composition of about 0.2 mole fraction of an additive the water network could become "saturated" with the additive. Further addition of the additive results in the formation of two
"microphases" a highly structured microphase consisting predominantly of water and a relatively disorder microphase containing mostly the additive molecules.

The question of the probable solute-additive interactions in an aqueous solution in regard to the structure and/or thermodynamic state of water in very complex. The additives may incorporate in the hydration shell of the solute and may alter the solute-water interactions even in the absence of a direct solute additive interaction. In particular, Kuharski and Rossy in a molecular dynamics study, simulated the incorporation of urea in the hydration shell or a non-polar solute. These authors have shown that interactions between water-water and water-urea molecules in contact with the solute were of somewhat stronger nature than that of interactions in the bulk solutions, although the enhancement was found to be smaller than in pure water. Numerous experimental observations may be explained by that an additive could build in into the structure of the hydration shell of a solute.

Essentially, all the experimental information reported in the enormous literature on the subject implies that the presence of an additive in water could alter the solvent properties of the aqueous medium in the solution relatively to those on pure water. It seems quite possible for the simplicity sake to attribute these alterations to a change in the water structure. Note once again that by the term of water structure was meant not only the space arrangement of water molecules but also the distribution of the energies of interactions between the molecules.

One of the attempts to quantify the structural changes in the solvent occurring in aqueous solution could be worthy of notice to illustrate the most typical difficulty. Ben-naim proposed to estimate the structural alteration in water by the change in the average number of H-bonds occurring in the solvent. This approach has led to many interesting finding described in various studies. This approach has led to many interesting findings described in various studies. The measurement however,
1.4 Hydrophile-Lipophile Balance (HLB)

The term Hydrophile-Lipophile Balance (HLB) first suggested by Clayton, refers to the balance in size and strength between the hydrophilic and hydrophobic parts of a surfactant molecule. The HLB value is an empirical number assigned to non-ionic surfactants on the basis of experiments carried out on surfactants. These HLB values range from 1 to 40, the low numbers generally indicating solubility in oil and the high numbers solubility in water.

Davies attempted to calculate HLB values by assigning an HLB contribution group number to each functional group in a molecule after studying the relative coalescence rates of stabilized oil droplets in water and water droplets in oil. The table below gives the group number characteristics of each functional group-

<table>
<thead>
<tr>
<th>Hydrophilic Group</th>
<th>Group number</th>
<th>Hydrophobic Group</th>
<th>Group number</th>
</tr>
</thead>
<tbody>
<tr>
<td>-SO₄Na</td>
<td>38.7</td>
<td>-CHH-</td>
<td>0.475</td>
</tr>
<tr>
<td>-COOK</td>
<td>21.1</td>
<td>-CH₂-</td>
<td>0.475</td>
</tr>
<tr>
<td>-COONa</td>
<td>19.1</td>
<td>-CH₃</td>
<td>0.475</td>
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<tr>
<td>-SO₃Na</td>
<td>11.0</td>
<td>=CH-</td>
<td>0.475</td>
</tr>
<tr>
<td>-N (tertiary amine)</td>
<td>9.4</td>
<td>-CF₂-</td>
<td>0.870</td>
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<tr>
<td>Ester (free)</td>
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<td></td>
</tr>
<tr>
<td>-COOH</td>
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<td></td>
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<tr>
<td>-OH (free)</td>
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<tr>
<td>-O-</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-OH (sorbitan ring)</td>
<td>0.5</td>
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