Abstract
Surfactant is an abbreviation for *surface-active-agent*, which literally means active at a surface. In other words, a surfactant is characterized by its tendency to adsorb at surfaces and interfaces, and of altering to marked degree the surface or interfacial free energies of those surfaces.\(^1\) Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, and plastics. Moreover, surfactants play a major role in the oil industry, for example, in enhanced and tertiary oil recovery.

A surfactant has two functional parts, namely, a hydrophilic (water soluble) or polar part, and a hydrophobic (oil soluble) or nonpolar part. They are amphiphilic, organic or organometallic compounds. The primary classification of surfactants is made on the basis of the charge of the polar head group. It is common practice to divide surfactants into the classes anionics, cationics, nonionics and zwitterionics. Surfactants belonging to the latter class contain both an anionic and a cationic charge under normal conditions. One of the most exciting developments in the field of surfactant chemistry is the emergence of the "gemini" surfactants. The term gemini, coined by Menger\(^2\), has become accepted in the surfactant literature for describing dimeric surfactants, that is, surfactant molecules that have two hydrophilic (chiefly ionic) groups and tails per surfactant molecule. These twin parts of the surfactants are linked by a spacer group of varying length (most commonly a methylene spacer or an oxyethylene spacer).
One of the fundamental properties of surfactants is that the monomers in solution tend to form aggregates, so-called *micelles*. Micelle formation, or micellization, can be viewed as an alternative mechanism to adsorption at the interfaces for removing hydrophobic groups from contact with water, thereby reducing the free energy of the system. It is an important phenomenon since surfactant molecules behave very differently when present in micelles than as free monomers in solution.

When surfactants are dissolved in water at low concentrations, physical properties of the solutions, such as surface tension, conductance, vapor pressure, and turbidity, indicate that little or no aggregation of surfactant occurs. However, as the concentration is increased, the behavior of such properties, and that of many others, changes dramatically over a relatively narrow range of concentrations. This range of concentration is known as *critical micelle concentration* (cmc). The cmc depends upon the nature of the polar group, the surfactant counterion, the length and the structure of the hydrophobic chain, solvent polarity and type, temperature, pressure, and pH.

At low surfactant concentrations, the micelles are usually spherical and the radius of the micelle is nearly equal to the length of the surfactant molecule. Upon increasing the surfactant concentration, spherical micelles become cylindrical and subsequently the cylindrical structure become hexagonally packed. If concentration is further increased, lamellar structures are formed. It is possible to induce a transition from one structure to another by changing the physico-chemical conditions such as temperature, pH, addition of salts, etc.
Information on the structural units that exist in surfactant solutions over the whole concentration range is important from both fundamental and practical points of view. At the fundamental level, it is important to relate the structure formed, such as spherical or rod-shaped micelles and various liquid crystalline phases, to the molecular architecture of the surfactant.

A simple model for surfactant aggregation in which the optimal aggregate size and shape are determined essentially from the packing ratio, $R_p$, are effective for predicting the micellar structure. This parameter relates the partial molecular volume of surfactant, $v$, the head group area of surfactant molecule, $a_0$, and the maximum chain length, $l_c$:

$$R_p = \frac{v}{a_0 l_c} \quad (1)$$

The theory predicts the formation of different types of micelles on the basis of the value of the parameter $R_p$. When $R_p < 1/3$, spherical micelles are formed and when $1/3 < R_p < \frac{1}{2}$ cylindrical and rodlike micelles are preferred. The micelle shape tends to be bilayer for $R_p > 1/2$ and when $R_p = 1$ vesicles are formed. For $R_p > 1$ reverse micelles may be obtained. The more hydrophilic the head group the larger will be $a_0$. The parameter $l_c$ is assumed to be a property primarily of the tail.

The packing ratio is affected by many factors including the hydrophilicity of the head group, the ionic strength of the solution, pH, temperature, and the addition of lipophilic compounds such as cosurfactants.
The more hydrophilic the head group, the stronger the repulsion and the larger will be $a_o$. The smaller the value for $R_p$, the smaller will be the micelle formed.

The salt serves to reduce the electrostatic interaction between the cationic head groups, thus reducing the effective area per head group and thereby promoting the growth of cylindrical aggregates at the expense of spherical ones. Two types of salts are typically distinguished: simple salts, which simply shrink the ionic double layer around each head group, and binding salts, which also reduces the surface charge by binding their counterions to the cationic micelle. Thus, binding salts, with counterions such as salicylate, tosylate, or anthranilate, tend to induce micellar growth at very low concentrations. The introduction of certain organic additives also promotes the sphere-to-rod transition and the continued growth of the rods to the same limit, at which point some of the rods apparently revert back to spheres or convert to disks, as evidenced by viscosity measurements. The availability of an organic additive/cosurfactant also suppresses head group repulsion and promotes a higher aggregation number in much the same manner as a counterion, but with a less marked decrease in the surface area occupied per surfactant monomer.

The combined presence of salts and organic additives produces a synergism (e.g., significant increase in viscosity) in micellar solution. This synergism was found to be dependent on the nature of the additives. It was further shown that presence of salt might change the conventional
solubilization site of a particular additive and thus produce micellar morphology of different kinds compared to the starting system.

Solubility of surfactants in solvent is, from simple thermodynamic arguments, predicted to increase on heating. However, for most of the nonionic surfactants in water, opposite behavior is observed: their solubility decreases with the increase in temperature. Above a certain temperature, known as lower consolute temperature or cloud point (CP), two isotropic phases are well defined: a dilute aqueous phase containing a low concentration of surfactant (surfactant lean phase), and surfactant rich phase. The mechanism of CP is still not very clear. The models that have been developed for the clouding phenomenon explain the mechanism by invoking critical concentration fluctuation, micellar growth, or micellar branching. The studies so far show that removal of interfacial water from the micellar surface is the key requirement for the clouding phenomenon in surfactant solutions.

Ionic surfactants show clouding in the presence of high salt concentration or large hydrophobic counterions. As such, aqueous solutions of tetra-n-butylammonium dodecyl sulphate (TBADS) exhibit CP. The work described in the thesis deals with studies on: (i) effect of various classes of additives on the CP of TBADS, (ii) structural transitions taking place in sodium dodecyl sulfate (SDS) solutions in the simultaneous presence of cationic hydrophobic salts and aliphatic organic additives, and (iii) effect of organic additives on the gemini micellar solutions in the presence of aromatic organic salts.
Chapter I is General Introduction wherein a detailed account of the behavior of surfactants, various phenomena exhibited by them, and the effect of additives are described.

Chapter II deals with the experimental details. Materials used, their purities, make, etc., are also given in a tabular form.

The micellar morphology in aqueous 0.2 M SDS solutions has been studied in the simultaneous presence of organic salts (anilinium hydrochloride, AHC; ortho-toluidine hydrochloride, oTHC; para-toluidine hydrochloride, pTHC) and aliphatic alcohols (n-butanol, C₄OH; n-pentanol, C₅OH; n-hexanol, C₆OH; n-heptanol, C₇OH), aliphatic amines (n-butylamine, C₄NH₂; n-pentylamine, C₅NH₂; n-hexylamine, C₆NH₂; n-heptylamine, C₇NH₂) and aliphatic hydrocarbons (n-hexane, C₆H; n-heptane, C₇H; n-octane, C₈H) by viscosity measurements under Newtonian flow conditions at 30 °C (Chapter III). Addition of alcohols and amines cause micellar growth, which is found to be dependent upon chain length of the additive and nature of organic salt counterions. It is observed that amines are more effective in increasing the viscosity of the system if added in pure 0.2 M SDS solution while SDS + pTHC system was found versatile when alcohols were added to this system. The increased viscosity or micellar growth is explained in terms of solubilization region of respective additive and the interaction of the additive with micellar surface and salt counterion present in the head group region. These additives are found effective in tuning the environment of the micelle which is reflected in viscosity behavior. Hydrocarbons are nearly ineffective in
inducing micellar growth and can be used as ‘micelle destroyer’ for the grown micelles. The results may find use in micellar ultrafiltration as well as in mimicking the natural cell, which has several aspects common with the micelle.

Chapter IV deals with the effect of anionic hydrophobic salts on cationic gemini surfactant in simultaneous presence of organic additives. Viscosity measurements have been performed to study the effect of addition of organics (alcohols, C₄OH–C₇OH; amines, C₄NH₂–C₇NH₂; hydrocarbons, C₆H, C₇H) to gemini surfactant bis(hexadecyldimethylammonium)butane dibromide (designated as 16-4-16) solutions in the absence as well as presence of aromatic acid salts (sodium salicylate, NaSal; sodium benzoate, NaBen; sodium anthranilate, NaAn) at 30 °C. When only salts were added to 16-4-16 solutions, the viscosity variation with each salt was different (although the surfactant and salt concentrations were of the same order) – NaSal was found to be the most efficient in increasing the viscosity. The behavior has been explained on the basis of different binding capacities of the counterions that influence the \( R_p \) to different extent. When organics were added in presence of the aromatic acid salts various interesting viscosity – [additive] profiles were observed. The data are explained in the light of solubilization sites of organic additives. It is found that a synergistic effect exists when C₅OH is added to 16-4-16 + NaSal system. Amines are less effective than alcohols while hydrocarbons are found only to decrease the viscosity due to conversion of grown micelles to swollen micelles.
The study may find application in formulations where thickening/thinning is desirable.

Chapter V describes the observance of clouding phenomenon in aqueous anionic surfactant TBADS in presence of different inorganic bromides (LiBr, NaBr, KBr, NH₄Br), inorganic nitrates (LiNO₃, NaNO₃, KNO₃, NH₄NO₃, Mg(NO₃)₂, Ca(NO₃)₂, and Sr(NO₃)₂), quaternary ammonium bromides (tetraethylammonium bromide, TEAB; tetrapropylammonium bromide, TPAB; and tetra-n-butylammonium bromide, TBAB), aliphatic alcohols (C₁OH, C₃OH–C₇OH), aliphatic amines (C₂NH₂, C₄NH₂, C₆NH₂, C₇NH₂), ureas/thioureas (urea, thiourea, monomethyl urea, dimethylurea, dimethylthiourea, tetramethylurea), carbohydrates (xylose, mannose, fructose, sorbose, arabinose) and amino acids (glutamic acid, histidine). Inorganic salts increase the CP followed by a decrease with the continuous addition of salt. The presence of salts provides additional counterions to the system which can be exchanged with TBA⁺ present at the micellar surface. In doing so, inorganic counterions would carry more water near the micellar surface and therefore increase in the CP is expected. At higher concentrations of added salts, the decrease in CP may be due to the micellar growth as additional counterions may screening out electrostatic interactions and be responsible for predominance of hydrophobic interactions. Divalent counterions are more effective in increasing as well as decreasing the CP. The effectiveness of divalent counterions may be due to their additional positive charge, and hydration, which can influence both the exchange (with TBA⁺) and screen
effect. In contrast to inorganic, quaternary counterions (TEA\(^+\), TPA\(^+\) and TBA\(^+\)) are less hydrated. Addition of TEA\(^+\) and TPA\(^+\) causes an increase in the CP. This may be due to the exchange of TBA\(^+\) with TEA\(^+\) or TPA\(^+\), and the closer interaction among the micelles would be disturbed and may be the reason of increase in CP. However, with externally added TBA\(^+\) (as TBAB), an opposite behavior (CP decrease) was observed. As the [TBA\(^+\)] increases in the system, one can expect more connections of micelles through butyl chains with the concomitant decrease in the CP.\(^{11(b)}\) The addition of aliphatic organic compounds causes both increase and decrease in CP depending upon their solubility (in water) and hydrophilic ranking. The additives of urea family also influence CP both ways depending on whether they are containing >C=O or >C=S moiety. The former mainly affects water structure while the latter can interact directly with the micelle. In doing so, thio compounds may compete with tetra-\(n\)-butylammonium counterion (TBA\(^+\)) for the space near the micellar surface. All sugars decrease the CP, which is in cognizance to their effect on the critical micellar concentration of surfactants. These observations are similar in form to the decrease in the water solubility of hydrophobic derivatives caused by sugars and reinforce the belief that water structure makers strengthen the hydrophobic interactions. The CP depression indicates a ‘salting out’ effect because the temperature range in which the single-phase solution prevails is reduced. Influence of amino acids on the CP is dictated by their acidic/basic nature. The overall effect of the additives is found to depend upon their ability to modify micellar morphology and/or structure of water.
References


