Chapter I

Introduction

I.1 SURFACTANTS

Twentieth century probably will be remembered for its continuing technology revolution that changed the life style of the human being. Rapid development of scientific insight, fabrication of new materials and invention of myriads of new sophisticated devices all occurred at a high pace. Miniaturization or Nanotechnology is one of the most important goals of this revolution. During this period, various structures have led to many micro- heterogeneous supramolecular systems that found wide applications in the field of science. In this class of structures, the one that are used in diverse research areas, from basic chemical kinetics to membrane mimetics in biological system is the so-called "SURFACTANT".

SURFACTANT, a contraction of term SURFace-ACTive AgeNT is a substance that, when present at low concentration in a system has the property of adsorbing onto the surfaces or interfaces of the system and thereby alter the surface or interfacial free energies of those surfaces or interfaces substantially. The term *interface* indicates a boundary between any two immiscible phases; the term *surface* denotes an interface where one phase is a gas, usually air[1].

Surface-active agents are organic substances having a characteristic molecular structure consist of two groups, one that has a very little attraction for the solvent, known as *lyophobic group* (*hydrophobic*), and the other that has a strong attraction for the solvent, called *lyophilic* (*hydrophilic*) group. The *hydrophilic* part is called the head group and the *hydrophobic* part is called the tail group, this combination is known as an "amphiphilic" structure. The two different *hydrophilic* and *hydrophobic* parts make the surfactant surface active in the sense that it adsorbs or accumulates at interfaces between polar and non-polar media, so that the head group is solvated in the polar medium and the tail group in the non-polar medium. A typical amphiphilic molecule consists of two parts: on the one hand a polar group which contains heteroatoms such as O, S, P, or N, included in functional groups such as alcohol, thiol, ether, ester, acids, sulfate, sulfonate, phosphate, amine, amide etc...On the other hand, an essentially apolar group which is in general a hydrocarbon chain of the alkyl or alkylbenzene type, some time with halogen atom.

Amphiphiles exhibit other properties than tension lowering and this is why are often labeled, according to their main use, as: soap, detergent, wetting agent, dispersant, emulsifier, foaming agent, bactericide, corrosion inhibitor, antistatic agent etc.

In an aqueous solution of a surfactant, there is distortion of the water structure by the hydrophobic group of the surfactant, and the resulting increase in the free energy of the system when it is dissolved, implies that less work is needed to bring a surfactant molecule compared to a water molecule to the surface. On the other hand hydrophilic group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The structure of the surfactant, therefore, causes not only adsorption of the surfactant at the surface and reduction of surface tension, but also orientation of the molecule at the surface, its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

I.1.1 NATURAL SURFACTANTS.

It is not an exaggeration to say that the life, as we know would not be possible without surfactants. Cell membranes are composed mainly of amphiphiles, which are self-assembled into a bilayer structure with the molecules oriented so that the hydrophilic groups are on the outside of the membrane and the hydrophobic groups avoid contact with aqueous regions by being packed closely together inside the membrane. Phopholipids are the surfactants that help to stabilize the emulsion in water and Bile salts e.g. sodium glycocholate etc are surfactants produced in the liver and stored in the gall bladder.

I.1.2 SYNTHETIC SURFACTANTS

Many operations and processes in both domestic and industrial situations rely on surfactants and, in most cases, these surfactants are synthetic. Synthetic surfactants may be produced from petroleum derived feedstock (e.g. alcohols, alkylbenzenes, alkylphenols) or natural raw materials (vegetable-and animal-derived oils and fats, fatty acids and alcohols, carbohydrates, etc.)

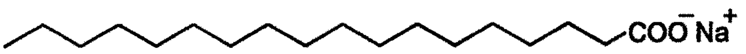
Because of their unique chemical structure and ability of self-aggregation, surfactants are used in numerous fields of industrial and commercial application. The most useful property of micelles is their ability to dissolve hydrophobic material in their interiors. This leads to the use of micelle-forming substance as detergents, and carriers for otherwise insoluble drugs[2], and in organic synthesis *via* micellar catalysis.[3] They are also used in food and dye stuffs, textiles, pesticides, tertiary oil recovery[4], paints, cosmetics, fire fighting etc. as well as in high technologies like electronic, biotechnology, viral and cancer research.

I.2 CLASSIFICATION OF SURFACTANTS

Surfactants are usually classified according to the nature of head group. The hydrophobic part of a surfactant may consist of one or several hydrocarbon chains containing from 8 to 20 carbon atoms; the chain may be saturated or unsaturated, linear or branched and may contain hetero (oxygen) atoms, aromatic rings, amides, esters or other functional groups. Based on the charge on the polar head group and its molecular structure, they have been classified as follows,

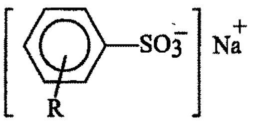
(1) Anionic Surfactants. The surface-active portion of the molecule bears a negative charge.

Sodium stearate

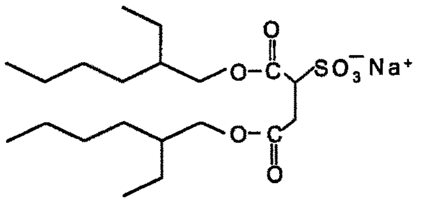


Sodium dodecyl sulphate (SDS)

Sodium dodecyl benzene sulphonate (SDBS)



Sodium bis (2-ethylhexyl) sulphosuccinate (AOT)

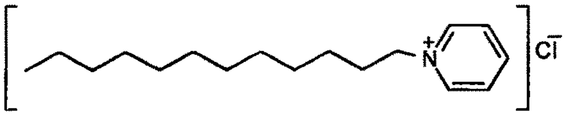


(2) Cationic Surfactants. The surface-active portion bears a positive charge.

Tetradecyl trimethyl ammonium bromide (TTAB)

Cetyl trimethylammonium bromide (CTAB)

Dodecyl pyridinium chloride

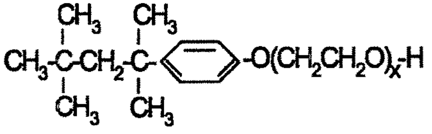


(3) Nonionic Surfactants. The surface-active portion bears no apparent charge.

Hexa oxyethylene n- dodecyl ether

$C_{12}E_6$ $C_{12}H_{25}(OCH_2CH_2)_6OH$

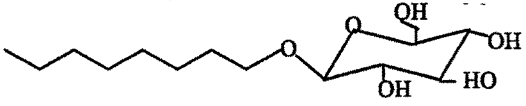
Poly oxyethylene t-octyl phenyl ether (Triton X 100)



$CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O(CH_2CH_2O)_x\text{-}H$

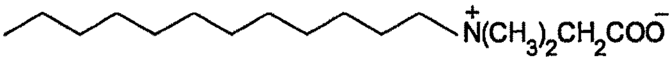
where x = 9 –10

Alkyl Poly Glycoside e.g Octyl β-D glucoside



(4) Zwitterionics. They are often referred as amphoteric. The surface-active portion bears both anionic and cationic groups on the hydrophobic moiety.

N-Dodecyl-N,N-dimethyl glycine



3-(Dimethyldodecylammonim)-propane-1-sulfonate

(5) Polymeric Surfactants. Block Polymers called Pluronics.

Pluronic – 85 $(OCH_2CH_2)_{50}(OCH_2CH_2CH_2)_8(OCH_2CH_2)_{50}$

(6) Gemini Surfactants. [5-7] These surfactants are made of two hydrophobic chains and two hydrophilic groups covalently attached through a spacer unit.

They may be different kind depending on the charge on head group

(i) Anionic Gemini

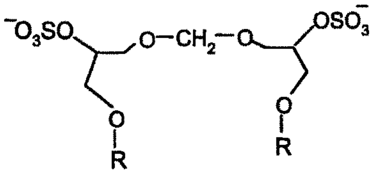
(ii) Cationic Gemini

(iii) Nonionic Gemini

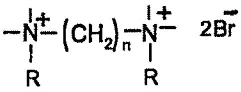
(iv) Zwitterinoinc Gemini

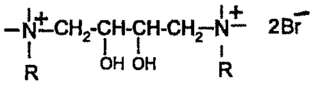
(v) Hetero Gemini

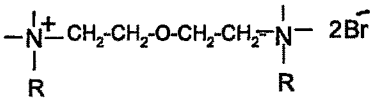
(i) Anionic Gemini [8-12]

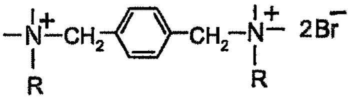


(ii) Cationic Gemini [13-22] bis(quaternary ammonium halide)


$-\underset{R}{\overset{|}{N^+}}-(CH_2)_n-\underset{R}{\overset{|}{N^+}}-\quad 2Br^-$

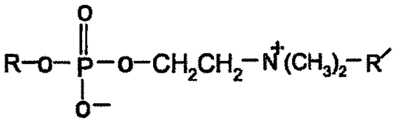

$-\underset{R}{\overset{|}{N^+}}-CH_2-\underset{OH}{CH}-\underset{OH}{CH}-CH_2-\underset{R}{\overset{|}{N^+}}-\quad 2Br^-$


$-\underset{R}{\overset{|}{N^+}}-CH_2-CH_2-O-CH_2-CH_2-\underset{R}{\overset{|}{N}}-\quad 2Br^-$



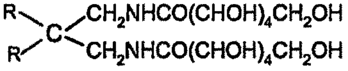
R is an alkyl chain where number of C atoms = 10-16. And in spacer, n= 4, 6, 8, 10, 12, 16

(iii) Zwitterioinc Gemini [23- 25]


$R-O-\underset{O^-}{\overset{O}{\overset{\|}{P}}}-O-CH_2CH_2-\overset{+}{N}(CH_3)_2-R'$

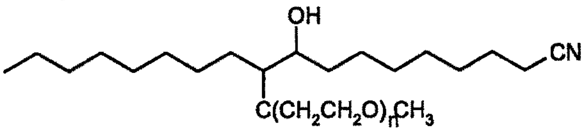
R and R ′ are an alkyl chain where number of C atoms = 6-14.

(iv) Nonionic Gemini [26] a disugar surfactant



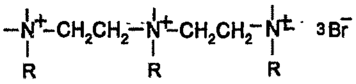
R is an alkyl chain where number of C atoms = 6

(v) Heterogemini Surfactant [27]



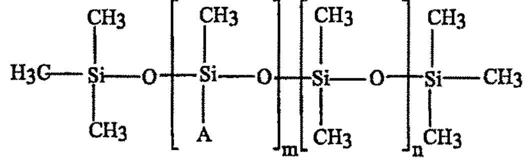
n=8,12,16

(7) Trimeric Surfactant[28-33] contain three hydrophobic and two or three hydrophilic groups connected by two spacer chains.


$-\underset{R}{\overset{|}{N^+}}-CH_2CH_2-\underset{R}{\overset{|}{N^+}}-CH_2CH_2-\underset{R}{\overset{|}{N^+}}\quad 3Br^-$

where R= 8,10,12

8) Silicone Surfactants[34-37]. They consist of a per methylated siloxane hydrophobic group (poly dimethyl siloxane) coupled to one or more polar groups.



$$H_3C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{A}{\overset{CH_3}{Si}}-O\right]_m\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

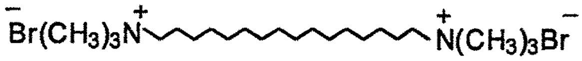
$A = (CH_2)_3-O-(C_2H_4O)_x-(C_3H_6O)_y-H$

m = polyether modified siloxane, x = ethylene oxide, y = propylene oxide

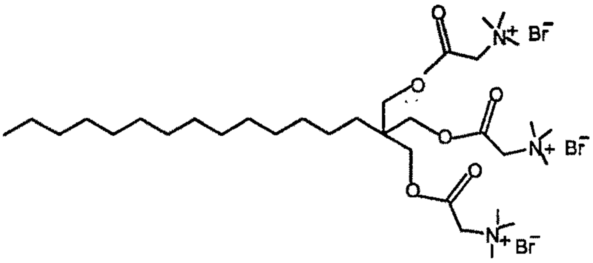
$[(CH_3)_3SiO]_2Si(CH_3)-CH_2CH_2CH_2(OCH_2CH_2)_8OH$

(9) Bolaform Surfactants. [38] They have two hydrophilic groups connected by a long linear polymethylene hydrophobic chain.

Hexadecanediyl-1,16-bis(trimethyl ammonium bromide)



10) Multiheaded Single-chain Surfactant. [39-41]



(11) Hybrid Surfactants. [42a] Contain a hydrocarbon and a fluorocarbon chain attached to the same hydrophilic group.

$(C_7H_{15})(C_7F_{15})CHSO_4^-Na^+$

$[OH(CH_2)_{11}N^+(C_2H_4)_2(CH_2)_2(CF_2)_5CF_3\ I^2$, or FHUB

(12) Catanionic Surfactant. Contain equimolecular mixture of cationic and anionic surfactants. No inorganic counterions.

$C_{12}H_{25}(CH_3)_3\overset{+}{N}\,.\,\overset{-}{O}S_4C_{12}H_{25}$

I.3 MICELLES

The fundamental property of surfactants is their ability to form aggregates when mixed with water. These compounds self assemble into a variety of microstructure like micelles, vesicles, liposomes, microtubes, bilayers, microemulsions etc. Among all these, micelle is the center of both fundamental and applied research interest due to its ever-growing applicability. The presence of micelle was originally first investigated by McBain[42b,43] and later by Hartley[44]. Micelles begin to form at a specific concentration called the critical micelle concentration, cmc.[45,46] McBain concluded that below the cmc most of the surfactant molecules are unassociated whereas in isotropic solutions, just above the cmc, micelles and surfactants coexist with concentration of latter changing very slightly as more surfactant is dissolved.

The process of surfactant clustering or micellization is primarily an entropy-driven process.[47,48] When surfactants are dissolved in water, the hydrophobic group disrupts the hydrogen bonded structure of water and therefore increase the free energy of the system. Surfactant molecules therefore concentrate at interface, so that their hydrophobic groups are removed or directed away from the water and the free energy of the solution is minimized. The distortion of the water structure can also be decreased (and the free energy of the solution reduced) by the aggregation of surface-active molecules into clusters (micelles) with their hydrophobic groups directed towards the interior of the cluster and their hydrophilic groups directed towards the water.

However, the surfactant molecules transferred from the bulk solution to the micelle may experience some loss of freedom from being confined to the micelle. In addition, they may experience an electrostatic repulsion from other similarly charged surfactant molecules in the case off surfactants with ionic head groups. These forces increase the free energy of the system and oppose micellization. Hence, micelle formation depends on the force balance between the factors favoring micellization (van der Waals and hydrophobic forces) and those opposing it (kinetic energy of the molecules and electrostatic repulsion). The explanation for the entropy dominated association of surfactant molecules is called the "hydrophobic effect".[49]

The micelles consist of limited number of surfactants, typically 50-150, forming a closed structure in order to minimize the contact between the surfactant's hydrophobic part and the water. It was suggested by Adam[50] and Hartley[51] that micelles are spherical in shape. G. S. Hartley,[51] one of the first to discuss the micelle structure, wrote in 1936

"The symmetrical asterisk form ....has no physical basis and is drawn for no other reason that the human mind is an organizing instrument and finds unorganized process uncongenial".

Figures 1.1 and 1.2 illustrate, two-dimensional and three-dimensional structure respectively of a spherical ionic micelle.

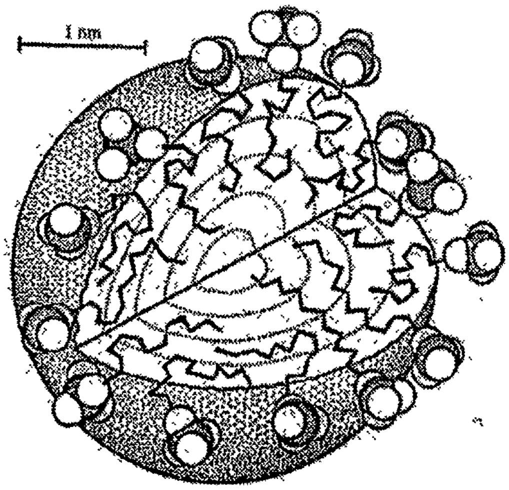


Figure I.1 A spherical micelle of ionic surfactant emphasizing the liquid like character with a disordered hydrocarbon core. (Ref. 54)

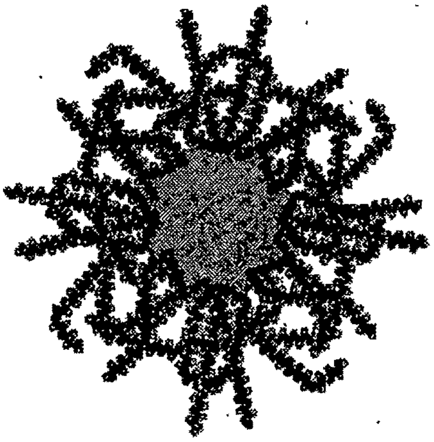


Figure I.2. Schematic representation of a nonionic micelle. (Ref. 56, p.95)

I.4 MICELLAR STRUCTURE

Micelles, unlike solid particles or rigid macromolecules such as DNA, are soft and flexible, i.e. fluid-like. This is because the forces that hold surfactant molecules together in micelles are not due to covalent or ionic bonds but arise from the weaker van der Waals, hydrophobic, hydrogen-bonding and screened electrostatic interactions. Thus if the solution conditions such as temperature, surfactant concentration, additives, *p*H of a surfactant solution is changed then these not only will affect the interaction between the aggregates but will also affect the intermolecular forces within each aggregates, thereby modifying the shape, size, aggregation number and stability of micelles. In general the shape of the micelle is dependent on the structure of the surfactant, typically the relative size of the head group and tail group. Ionic surfactant from smaller micelles (aggregation number ~10-70) than nonionic surfactants ($N_{agg} \geq 100$). This is because the electrostatic repulsion between ionic head-groups is greater than the steric repulsion between non-ionic head groups.

The structure of a micelle could vary form spherical to rod- or disc- like to lamellar in shape. In concentrated solution (much above the CMC), lamellar micelles form, such that water molecules occupy the region between parallel sheets of surfactant. Micelles may also form long cylinders packed together (known as lytropic mesomorphs or liquid crystalline phases) at high surfactant concentrations[52,53]

Israelachvili[54] has shown that various structure of a surfactant solution can be expressed in terms of critical packing parameter, CPP defined as

$$CPP = V_h/l_c a_0,$$

where V_h, lc and a_0 are the volume occupied by the hydrophobic group in the micelle core i.e

$$V_h = 27.4 + 26.9\, n_c\, Å^3,$$

where n_c is the number of carbon atoms in the hydrocarbon chain of the surfactant molecule, l_c is the length of the hydrophobic group in the core. i.e $l_c = 1.5 + 1.265\, n_c$ Å and a_0 the area of cross section occupied by hydrophilic group at micelle solvent interface respectively.[55]

Spherical micelles will be formed if CPP<1/3. As CPP increases, i.e as the relative size of the hydrophobic part increases, the curvature of the aggregates will decrease and disc-, tablet- and rod like micelles are formed e.g. hexagonal [1/3 < CPP< 1/2], lamellar [CPP ≈1] and cubic [CPP ≥ 1] phases are possible.[56] A schematic representation of different kind of micellar structures and their dependence on the critical packing parameter is depicted in Figure. 1.3.

However for dilute solution, the spherical micelles are generally envisaged.

The spherical micelles have the following properties,[57]

(a) the association unit has radius approximately equal to the length of the hydrocarbon chain

(b) there are 50-100 monomers in micelle and this number increases as the hydrocarbon chain length increases

(c) the counter ions are bound to the micelles of ionic surfactants, thus reducing its mobility compared to its nonionic counter part

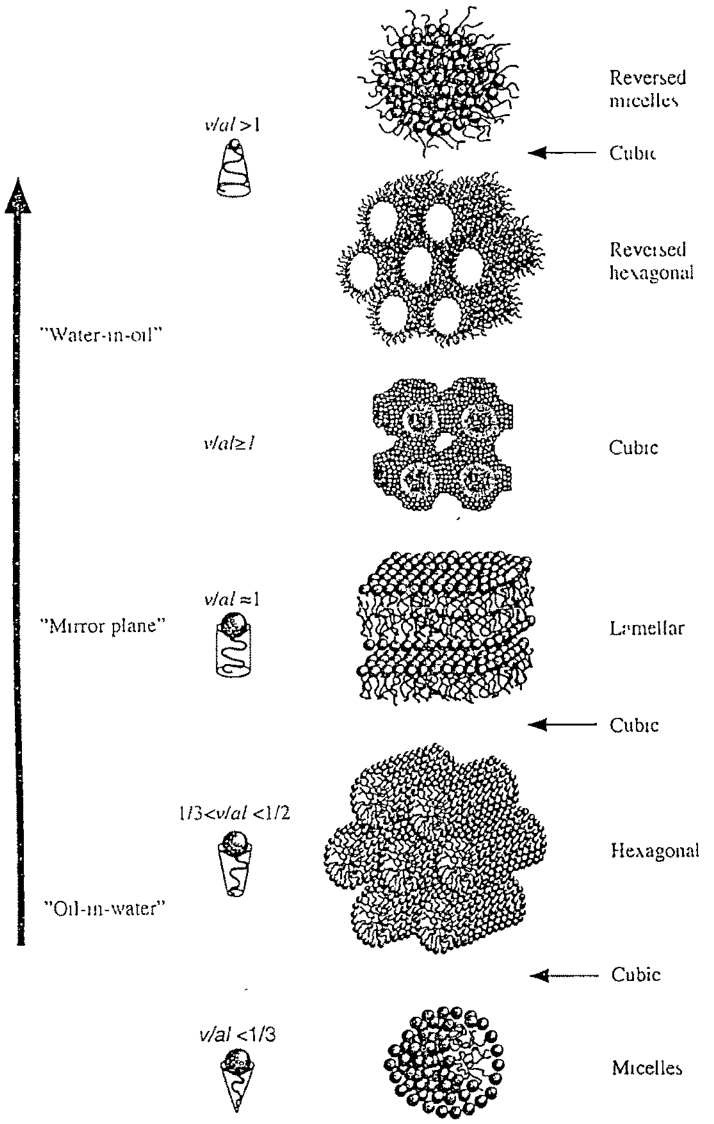


Figure I.3. Critical Packing Parameters (CPP) of surfactant molecules and aggregate structures due to geometrical reason. (Ref. 56 p.84)

(d) due to higher association number of surfactant monomers, micellization occurs over a narrow range of concentration

(e) the micelle interior has essentially the properties of liquid hydrocarbon as a result of which it solubilizes water insoluble organic molecules.

As mentioned earlier, apart from spherical micelles different shapes of micelles are known. They are i) elongated cylindrical rod like micelles with hemispherical ends (prolate ellipsoids); ii) large, flat lamellar micelles (disc like extended oblate spheroids) and iii) vesicles, almost spherical structures consisting lamellar vesicles arranged in one or more concentric spheres

Surfactants in a given solvent aggregate to form micelles, though the micelle formation is dependent on the type of solvent.[58] In aqueous medium, the surfactant molecule gets oriented in such a way that the polar heads are towards the solvent and the hydrocarbon groups away from it forming a part of micelle. Such micelle is termed as a "normal micelle".

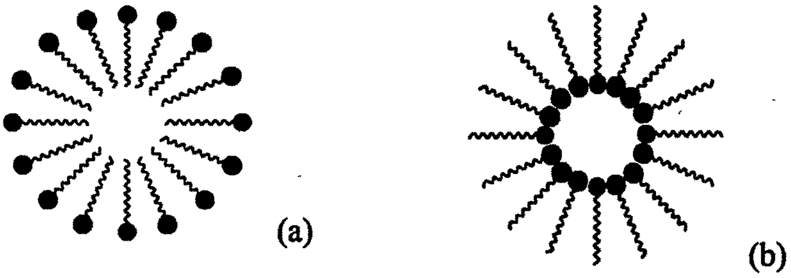


Figure I.4. A diagrammatic representation of micelle (a) normal micelle (in aqueous medium) and (b) reverse micelle (in non-aqueous medium)

Whereas in non-polar/non-aqueous medium, the lipophile attract the hydrophobic parts and forces the hydrophilic heads away, which then are held together by dipole-dipole interactions and lead to micelle core surrounded by hydrophobic groups in contact with the solvent, such micelles are termed as "reverse or inverted micelles". Both types of micelles are thermodynamically stable and are comparable dimensionally. Diagrammatic representations of a normal and reverse micelle are shown in Figure 1.4.

I.5 MICELLAR SHAPE

The generalized structure of a typical ionic micelle containing a liquid core formed by the associated hydrocarbon chain with the fully ionized head groups projecting out into the water. Immediately surrounding the core is the stern layer, which contains not only the ionic head groups but also counterions. The stern layer constitutes the inner part of the electrical double layer surrounding the micelle. The outer, more diffuse layer, which contains the remaining counterions, is termed as Gouy-Chapman layer. The core and the Stern layer form the micelle with some charge. The surface potential of the micelle is the electrophoretic Zeta potential.

In polyoxyethylated non-ionic micelles the core is surrounded by a layer composed of the polyoxyethylene chain to which solvent molecules may be hydrogen bonded. This region of the micelle is often termed the palisade layer. Palisade layer is also present in ionic micelles.

Recent years have seen a renewed interest in the investigation of the nature of the micellar regions as more sophisticated experimental techniques have become available like small angle neutron scattering (SANS), small angle X-ray Scattering (SAXS). An understanding of the detailed nature of the micellar microenvironments is important in understanding the ability of the micelles to act as solubilizing agents and for the prediction of the location of the solubilizate molecules within the micellar entity.

Since micelles are dynamic structure with a liquid core, it is probably unrealistic to regard them as rigid structures with a precise shape. It is, however, instructive to consider an average micellar shape. For the purposes of interpretation of experimental data it is usual to assume that the micelles are spherical in shape. Several author[s59-71] have shown from geometrical considerations that most of the common surfactants with a single unbranched chain cannot form truly spherical micelles. Tanford[68] has proposed that the distortion of the micellar shape into an ellipsoid is the simplest way of incorporating a larger number of molecules into micelles. The semiminor axis (b=c) of such an ellipsoid would not exceed the maximum extension of the hydrocarbon chain. No such limitation would exist for the semimajor axis (a), which could now increase to provide the additional volume. Only small values of the axial ratio (a/b) were necessary to allow a sufficient increase in the permitted aggregation number such that the most hydrocarbon chain surfactants may be accounted for.

The Triton X-100 micelle is considered by many workers to be spherical,[63,64] From geometrical considerations, Robson and Dennis[65] have shown, however, that a spherical micelle would be possible only if several oxyethylene chains were embedded in the hydrophobic core (Fig 1.5 a). These authors consider that an oblate (Fig 1.5 b) rather than prolate (Fig 1.5 c) micelle would be most consistent with intrinsic viscosity measurements and volume calculations. Small angle X-ray scattering measurements,[66] conductivity and viscosity measurements[67] were also more consistent with an oblate ellipsoid of revolution rather than a prolate equivalent.

A disc-like (oblate) shape has been assigned to the micelles of two n-alkylpolyoxyethylene glycol monoethers, $C_{12}E_6$ and Lubrol WX ($C_{17}E_{16}$) from sedimentation and viscosity data respectively[68]. From theoretical considerations, Tanford has maintained that, except when head group repulsion is very strong, oblate ellipsoids are thermodynamically favoured over prolate ellipsoids for most micelles. Micelar shape is affected by such factors as concentration,[72] temperature,[73] Pressure,[74] ionic strength,[75] Charge,[76] hydrocarbon chain length,[77] the nature of the head group,[78-80] types of the counterions[81] and the presence of additive.[82-88] It is not uncommon for micelle shape to undergo a transition with increase in one of these parameters from a near spheroidal shape to a more asymmetric form. ^{14}N nmr relaxation measurements on aqueous solution of cetyltrimethylammonium bromide (CTAB) have shown an increase in correlation time with concentration which has been interpreted in terms of an increase micellar asymmetry; it was concluded that rod like aggregates were formed at higher concentrations.[89] These finding are in agreement with earlier small-angle

X-ray scattering measurements on CTAB solutions which indicate a transition from spherical to rod-shaped micelles at a concentration of ~0.15M.[90]

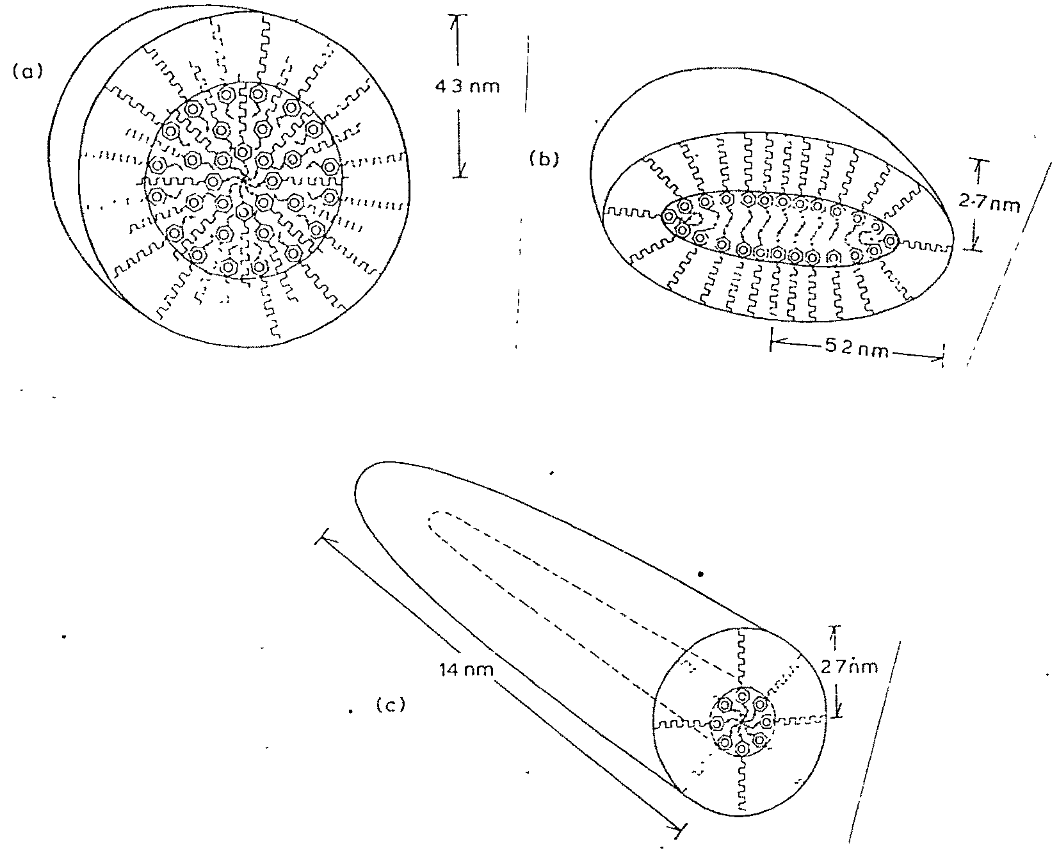


Figure I.5 Schematic diagrams of one-half of the micelle of Triton X-100 based on geometrical calculation by Robson and Dennis[65] for (a)Spherical, (b) oblate, and (c) prolate micelle models. The spherical model necessitates instruction of the oxyethylene chains into the micellar core.

Small-angle neutron scattering indicates that 16-3-16 gemini surfactants at 2.5-10mM and 30°C form disk like micelles.[91a] Upon further heating to 45-70°C, the disk converts into a rod (with a length of 500Å and a radius of 27 Å) owing, probably, to subtle changes in the effective charge per monomer. With spacer of 5 or more, micelles are prolate-shaped. Thus, spacer length controls micelles shape more than it does CMC.[45] Maiti and Chowdhury[91b] had fitted theoretical modeling of both ionic and nonionic geminis, with both hydrophobic and hydrophilic spacers, using Monte Carlo simulations and conclude that (i) short hydrophobic spacer are grossly nonspherical micelles ("threads"), whereas long hydrophobic space lead to rod like micelles, (ii) micelles with hydrophilic spacers are more or less spherical.

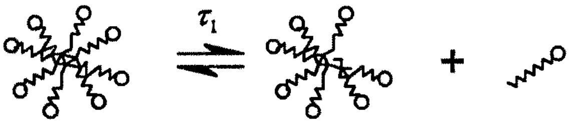
I.6 DYNAMIC ASPECTS OF MICELLE FORMATION

Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with individual surfactant molecules that are constantly being exchanged between the bulk and the micelles. The micelles are themselves continuously disintegrating and reassembling.

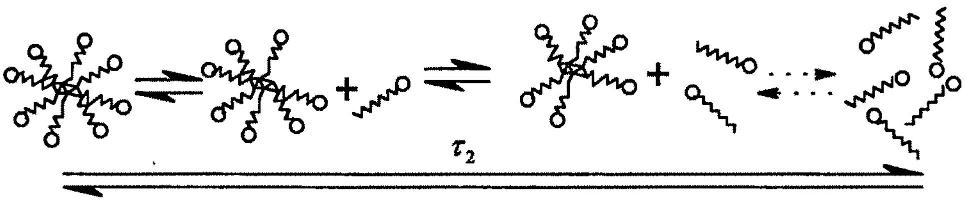
Micelles form and break up very rapidly (estimated relaxation times range from 10^{-2} to 10^{-9} s). The rate of these processes, interpreted in terms of a relaxation time (τ). Transient methods, as pressure-jump, and temperature-jump give values of τ ranging from 10^{-2} to 10^{-5}s, while steady-state methods, such as nmr, esr, and ultrasonic absorption, always gives less than 10^{-5}s.[92,93] This wide range of relaxation times suggests that at least two different relaxation processes are being observed.[94-104] The first is a fast relaxation process referred to as τ_1(generally of the order of microseconds), which is associated with the quick exchange of monomers between micelles and the surrounding bulk phase. This process considered to be the collision between surfactant monomers and micelles. The second relaxation time τ_2(of the order of milliseconds) is attributed to the micelle formation and dissolution process (i.e., the lifetime of the micelle). It has been shown that in certain surfactants such as nonionic surfactant and mixed surfactant systems τ_2 can be as long as minutes. For example, the τ_2 of a 0.80mM solution of nonionic surfactant Synperonic A7 is 150s [96]

Figure 1.6 shows the two characteristic relaxation times, τ_1 and τ_2, associated with micellar solution. Micelle formation and disintegration is analogous to the equilibrium between water and water vapor at a given temperature and pressure. Under equilibrium conditions, the rate of micelle formation is equal to the rate of disintegration into surfactant monomers.

Micellar relaxation kinetics shows dependence on temperature, pressure, and concentration, as well as on the addition of other species such as short-chain alcohols. It was shown that the τ_2 of an SDS micelle decreases with increased concentration of C_1-C_5 alcohols[105]. The two relaxation time can be used to calculate two important parameters of a micellar solution: (i) the residence time of a surfactant molecule in a micelle and (ii) the average lifetime or stability of a micelle.



Fast relaxation time, microseconds



Slow relaxation time, miliseconds

Figure I.6. Mechanisms for the two relaxation times, τ_1 and τ_2 for a surfactant solution above CMC.[96]

For many years researchers tried to correlate the relaxation time, τ_2, with equilibrium properties such as surface tension and surface viscosity, but no correlation was found. However, a strong correlation of τ_2 with various dynamic processes such as foamability, wetting, bubble volume, emulsion droplet size, and solubilization rate of benzene in micellar solutions was found by Shah and co-workers[96,104] Shah et al.[104] concluded that SDS solution exhibit maxima in (i) micellar relaxation time, (ii) single film stability, (iii) bubble volume, and minima in (i) formability, (ii) frequency of bubble generation properties at 200mM concentration due to maximum stability of SDS micelles at this concentration. He also stated that most of ionic surfactants may exhibit such a characteristic concentration at which the micellar stability will be maximum due to increase in coulombic repulsion and reduction in intermicellar distance.

Micelles of nonionic surfactants show a much higher relaxation time (τ_2) than those of ionic surfactants, presumably because of the absence of ionic repulsion between the head groups. The relaxation time for Triton X-100 (0.4mM), $C_{12}E_8$ (0.4mM), $C_{12}E_5$ (0.8mM), Tween 80 (0.49mM), and Brij 35 (0.50mM) nonionic surfactant micelles are 3.5, 4, 10, 8-10, 80s respectively.[104]

The micellar relaxation time for nonionic surfactant can also be obtained by spectroscopic technique using different dyes or fluorescent compounds, like Merocynanine, Eosin, Rhodamine, and Sudan. There is an appreciable change of extinction coefficient depending on whether the dye resides inside or outside the micelle in the aqueous phase.[106] This effect is also used to determine the CMC of nonionic surfactants.[107,108]

The kinetics of surfactant exchange between dimeric surfactant micelles and intermicellar solution has also been investigated. Dimeric surfactants with short alkyl chains, 8-6-8,2Br- and 8-3-8,2Br-, were found to behave similarly to their monomeric counterparts.[21] The kinetics of the formation and breakup of dimeric surfactant micelles has not been investigated by direct chemical relaxation techniques. Rheological investigation of fairly concentrated solution of 12-2-12,$2Br^-$ thread-like micelles yielded micelles lifetime in the range 0.1-10 s.[84b]

I.7 CRITICAL MICELLE CONCENTRATION (CMC)

Amphiphiles have a characteristic property of adsorbing at interfaces and thereby lowering the interfacial energies. An alternative to the crowding at the interface, as the surfactant concentration is increased is provided by the formation of small aggregates or micelles in the bulk of the solution. The concentration at which micelles first appear in solution is termed the critical micelle concentration (CMC). Almost every physicochemical property of a surfactant are solution varies with the concentration of surfactant. [217b] The physical properties of surface-active agents differ from those of smaller or non-amphiphilic molecules in one major aspect, namely the abrupt changes in their properties above a certain critical concentration[72] termed as the critical micelle concentration. The physical properties, which undergo abrupt changes and those, which are useful in determination of cmc, include, equivalent conductivity, surface tension, osmotic pressure, light scattering intensity, self-diffusion, solubilization, magnetic resonance and microviscosity. Figure 1.7 illustrates the variation in a wide range of physico-chemical quantities of aqueous surfactant solutions around the critical micelle concentration.

One can clearly observe that over a narrow range of concentration the physical properties of the solutions suffer a discontinuity in their variation with concentration. This sudden change in their bulk properties corresponds to the formation of micellar aggregates and hence is used to determine the CMC of surfactant solutions. However, it is worth mentioning that this changes occurs over a narrow concentration range rather than at a precise point and the magnutitude of the CMC obtained depends on the property being measured though in most cases all values fall within the narrow range whatever the method is.

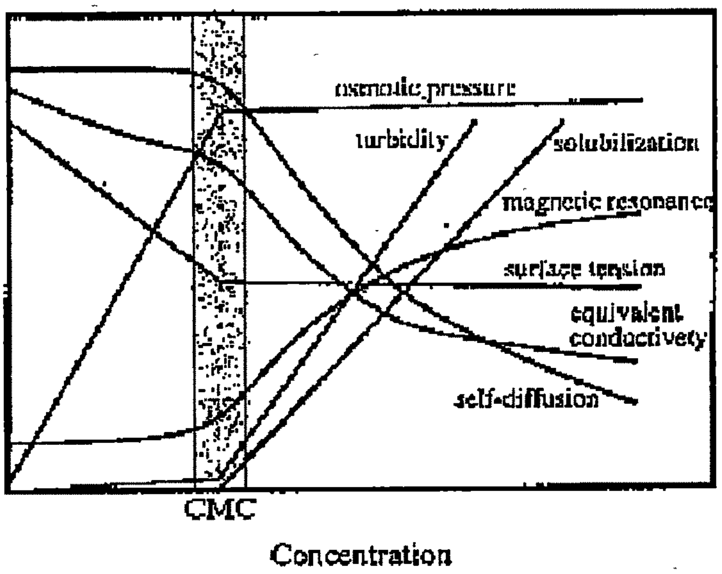


Figure I.7 Schematic representation of concentration dependence of physico-chemical properties for solutions of surfactant. The shading emphasizes the fact that the CMC is not necessarily sharply defined. (Ref 56 p. 36)

In principle any of the physical properties illustrated in Figure 1.7 could be used to determine the CMC but some of them have become popular because of their convenience and reliability. Two widely used physical properties are the surface tension and specific conductance.

The surface tension of a liquid is the non mechanical work required to create unit area of surface. A surfactant solution has a surface populated by adsorbed molecules in a state of lower free energy than those in the bulk solution. One would therefore need less work to create unit area of surface on a surfactant solution compared with that needed to create unit area for pure solvent. That means the adsorption of surfactant at the air/water interface lowers the surface tension of water. Near the CMC the surface gets saturated and hence the surface concentration remains constant above the CMC. This results in a nearly constant value of surface tension once the micelle starts forming. Thus a plot of surface tension versus log (concentration) shows a break corresponding to the CMC.

Another popular way of measuring CMC of ionic surfactants is from conductivity studies. Below CMC ionic surfactants dissociate in the solution and behave like conventional electrolytes. Above CMC there will be condensation of the counter ions on the micellar surface, which results in a large decrease in the equivalent conductivity. In other words, micellar solutions contain less number of charge carriers than the equivalent number of fully dissociated monomers. Thus a plot of conductivity versus concentration shows a break corresponding to the CMC due to decrease in the slope of the curve above CMC. The ratio of the two slopes above and below CMC gives an estimate of the degree of micelle ionization. The conductivity method is quite precise for ionic surfactant though its sensitivity decreases when excess electrolytes are present.

Each surfactant molecule has a characteristic value of cmc at a given temperature and it is the simplest mean of characterizing the colloid and surface behaviour of a surfactant solute, which in turn determines its industrial usefulness and biological activity, and also gives a measure of the structurally interesting solute-solvent and solute-solute interactions

I.8 FACTORS AFFECTING CRITICAL MICELLE CONCENTRATION

Since the properties of solutions of surface-active agents are very sensitive to the external parameters, the properties are influenced or tuned to desire range and application by altering the conditions. The CMC and the aggregation number, N_{agg} are two important parameters on which the practical applications of amphiphilic substances largely depend. Often a low CMC and high N_{agg} are desired. Many investigations have been concerned with determining the values of CMC in various surfactant systems. A great deal of attention was given in on elucidating the various factors that determine the cmc in aqueous solution. Among the factors known to affect the CMC in aqueous medium are, structure of the surfactant,[109-112] nature of the polar head group,[41,110,112] counter ion,[113-115] temperature,[116-118] pressure,[119] *p*H,[120-122] presence of electrolytes,[123-125] polar[126] and non-polar additives[127] etc.

I.8 (a) Surfactant Structure

Depending on the molecular structure and type, a balance between hydrophilicity and hydrophobicity exists in the surfactant molecules. This is called hydrophilic-liphophilic balance (HLB). Griffin[128] has suggested empirical numbers ranging between 0 to 40 for various groups known as HLB number. The HLB number of a surfactant molecule is calculated from the structure of the molecule; in some cases, it is based on experimental emulsification data.[1] HLB number is important in categorizing surfactant as emulsifiers, detergents, wetting agents, solubilizing agents, micelle-forming type etc.[129]

Little[130] found the linear relation between the HLB and CMC values of the surfactants (Figure 1.8).

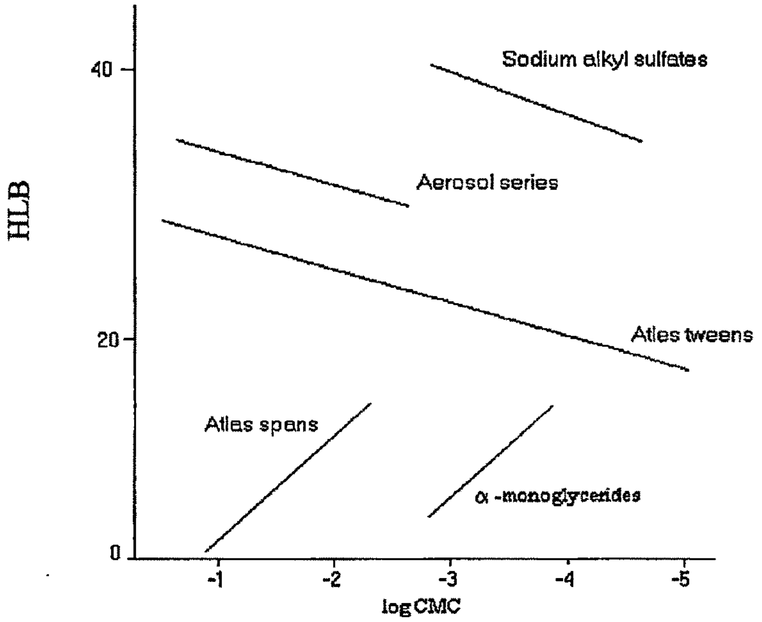


Figure I.8 The linear relation between the logarithm of the CMC and HLB for a number of homologous series. Aqueous solutions have negative slope and nonpolar solution have positive slopes.[130]

However, in general, in aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophobic tail increases to about 16.[131] As a general rule for ionic surfactants with one hydrophilic group, the cmc is halved by the addition of one methylene (-CH_2) group.[132] But for nonionic and zwitterionic surfactants, the magnitude of decrease in cmc is much larger. Chain branching, unsaturation of hydrophobic chain also has an influence on cmc.[107] The cmc values increase with increase in the number of head groups of surfactant.[41] If the chain length of hydrophobic group exceeds more than 18, the effect on cmc is limited as coiling of these long chains occur in water.[133]

Introduction of polar groups such as –O- or –OH in to the hydrophobic group causes a significant increase in cmc. Also, the surfactants with bulky hydrophobic/hydrophilic group delay the micelle formation due to steric factors. The replacement of a hydrocarbon based hydrophobic group by a fluorocarbon based one with the same number of carbon atoms decreases the cmc.[1] However, the replacement of terminal methyl group of a hydrocarbon based hydrophobic group by a trifluoromethyl group causes the cmc to increase.

In general, for the same number of carbon atoms the order of CMC in different kind of surfactants are ionic> zwitterionics> nonionic surfactants. Dimeric or Gemini surfactants have much lower values of cmc (~100 times) than the conventional surfactants.[45,46] The cmc values of dimeric surfactants have been found to be dependent on the length, nature (hydrophilic, hydrophobic) and flexibility of spacer.[135] For the series of quaternary ammonium surfactants [$C_{12}H_{25}N^+ (R)_3Br^-$], the cmc decreases as the length of alkyl chain (R) increases because of the corresponding increase in hydrophobicity.[1,113]

In the case of polyoxyethylene nonionics of type $C_{12}E_n$ (n= 4, 6, 8), the cmc values increase as the ethylene oxide content increases,[136] whereas for the surfactants of type C_nE_8, (n=9-15) the cmc decreases as the number of carbon atoms increases.[137] Rosen[137] has reported an increase in cmc with increase in hydrophilicity for C_nE_m (m= 1-8) and p-tert octyl phenoxy poly(ethenoxy ethanol) respectively.

In conventional ionic surfactants in aqueous solution, the increased binding of the counter ions causes a decrease in cmc of the surfactant. Thus the counterion with higher polarizability decreases the cmc more. Sepulveda et al[113] have reported the cmc values for hexadecyl and tetradecyl trimethyl ammonium micelles with various counter ions. Bahadur et al[114] reported the influence of valence of counter ion on the mixed anionic-nonionic system and they observed that the counter ion with highest charge density and small size decreased the cmc more. As the hydrophilic group is moved from a terminal position to a more central position, the CMC increases[1].

In the case of gemini surfactant they are more responsive to tail length than conventional surfactants. Increasing the tail length by four carbon atoms in a conventional cationic surfactant lowers the CMC 16-fold.[138] The variation in CMC with increasing chain length of hydrophobic part is linear i.e. CMC decreases with increasing chin length. However the plot of CMC vs spacer shows a maximum at around spacer 5 or 6, irrespective of the values of chain length between 10 to 16.[5] This peculiar behavior of the gemini surfactants as spacer < 5 was attributed to a change of the spacer conformation as spacer length is progressively increased, to its resulting effect on the hydration of the head groups and on the orientation of the alkyl chain.[5] The linear decrease of the CMC upon increasing spacer at >10 is due to the progressive penetration of the spacer in the micelle hydrophobic core.[5]

I.8 (b) Additives

The presence of an additional component in the surfactant solution alters the micellization process to a greater extent especially in two ways[139,140] i) through specific interaction with the surfactant molecules, ii) by changing the solvent nature.

The additives may be distributed between aqueous and micellar phase and may accumulate both in the palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. Electrolytes generally decrease the

CMC,[141] nonelectrolytes may increase or decrease,[142-144] some organic co-solutes which when present in some greater amounts may even cause disappearance of the micelles.[145]

Numerous studies have been reported on the effect of additives on the micellar properties of surfactants. Innumerable investigations on the study of the influence of electrolyte on the micellar properties of surfactants have been reported by several researchers.[139,146-149] The presence of electrolyte has more pronounced effect on the cmc of anionic and cationic surfactants. The presence of electrolyte reduces the thickness of the ionic atmosphere surrounding the polar head groups and consequently decreases the repulsion between them. Somasundaran et al[149] have reported the cmc values for sodium dodecyl sulphate (SDS) in presence of various electrolytes viz. NaCl, Na_2SO_4, LiCl, CsCl, Cs_2SO_4, $MgCl_2$, $MgSO_4$ and $Na_3(PO4)_2$. All these electrolytes decrease the CMC of SDS. Similar studies on the effect of electrolyte on micelle formation have also been reported by Mukerjee et al.[139] Abe et al[146] have reported the effect of different electrolytes (NaCl, NaOH and HCl) on the micelle formation of mixed amphoteric-anionic surfactant systems and they observed that the cmc values of mixed surfactant systems are much smaller than those of systems including NaCl. They concluded that the inorganic electrolytes affect the magnitude of hydrophobic-hydrophilic interactions between the constituent surfactant molecules in the mixed micelles. Goddard[150] and coworkers studied the effect of alkali metal salts and some quaternary ammonium salts on the cmc of SDS and found that the ability of alkali metal cations to decrease the cmc increases with decrease in the size of the hydrate cation.

Engberts et al[151] reported that the sodium salts decrease the cmc in the order $Cl^- < Br^- < NO_3^- < I^-$ for the surfactant 1-methyl 2-dodecyl pyridinium iodide. The order of decrease is in accordance with the lyotropic series of inorganic anions. Other than the electrolytes, organic additives are also known to influence the micellization behaviour of surfactants. Organic additives affect, either by being incorporated in to the micelle or by modifying solvent-solute interactions. Short chain polar compounds like dioxane and ethanol at low bulk phase concentrations depress the cmc, but the effect is too small and this is because in these compounds the adsorption probably occurs on the surface of micelle, close to the hydrophilic head.[152,153] The studies on effect of alcohols on micellar properties of surfactants were initiated by Ward.[154] He found that the CMC values of SDS passes through a minimum on addition of ethanol. Such behaviour was confirmed later for the first three homologous alcohols in various micellar systems. Candau et.al [155] show that alcohols may be distributed between aqueous and micellar phase and may accumulate both in palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system.

Alcohols also exhibit the typical characteristics of surfactants thus earning the appellative of cosurfactants. Zana[156] and co-workers have reported extensive studies on the effect of linear chain length alcohols on cmc of cationic surfactant tetradecyl micelles. It was found that long chain alcohols always decreased the value of cmc. Further contribution to the understanding of water-surfactant – alcohol systems were made by Shinoda,[157] Emerson and Holtzer,[158] Larsen and Tepley,[159]. Extensive studies on the effect of linear alcohols (ethanol to hexanol), on cmc, micellar molecular weight and degree of ionization of micelles of homologous alkyl trimethyl ammonium bromides have been reported by Zana and coworkers.[160-165] Treiner and coworkers have widely studied the partitioning of alcohols and other organic solutes in micellar solutions from cmc determinations.[166-171] Recently Gonzalez-Perez et al[172] studied the cmc and degree of ionization of micelles of tetradecyldimethylbenzyl ammonium chloride in aqueous solution of butanol and benzyl alcohol at different temperatures. They observed that benzyl alcohol influences the cmc values more strongly. The cmc values for both the surfactants decrease linearly with the molarity of the butanol, whereas in case of benzyl alcohol, peculiar breaks appear on both plots in C_{14}BCl and C_{14}TBr. The effect of other organic solvents like glycerol, hydrazine, amines and esters has also been well studied.[172-176]

Urea and its derivatives are well known water structure breakers and protein denaturants.[177,178] Since, Bruning and Holtzer[179] first demonstrated that urea disrupts micelles, many investigators reported that cmc of ionic and nonionic surfactants significantly increase with addition of urea in aqueous solutions.[180,181] Two different mechanisms were proposed to explain urea action on aqueous solutions (a) urea acts as a water structure breaker (indirect mechanism) and (b) urea participates with the solvation of hydrocarbon chains in water by replacing water molecules in the hydration shell of the solute (direct mechanism). However, recently a computer simulation of urea action in aqueous solution showed negligible influence of urea on the water structure, rather it weakens the water/water interaction by replacing several water molecules from an apolar solvation shell.[182,183]

Bakshi et al [184]registered the decrease in cmc of SDS and DTAB by 0.17M glycine by 7.4% and 10.4% respectively. The authors concluded that the cmcs of both SDS and DTAB decreased upon the addition of alanine, valine and methionine. However they found that the effect of these additives were much stronger in the case of DTAB rather than in the case of SDS.

Some other additives that markedly influence the aqueous solution properties are xylose, dextrose, fructose, sucrose and poly ethylene glycol; which are highly hydrophilic and water structure formers. Sulthana and coworkers[185-188] have extensively studied the effect of poly ethylene glycol, acetamide, sucrose as well as urea on micellization of nonionic, anionic and anionic/nonionic mixed surfactant system. They observed that the cmc of SDBS & mixed anionic/nonionic (SDBS/$C_{12}E_{10}$) surfactant system increased in the presence of additives. However, it was found that the cmc of $C_{12}E_{10}$ as well as Myrj 45 decreased in the presence of additives.

Maeda [189] has extensively studied the effect of change of *p*H on stability, aggregation number and titration properties of dodecyldimethylamine oxide (DDAO) surfactant. The author emphasized the formation of hydrogen bonds between the cationic-nonionic and cationic-cationic species. The effect of pH on other surfactant like cationic[190] hexadecyltrimethyl ammonium bromide (HTAB) and amphoteric-anionic[191] N,N-dimethyl N-lauryl lysine (DMLL)-sodiumdodecyl sulphate (SDS) were also studied. Herrann[192] showed that dimethyl dodecyl amine oxide (DDAO), behave nonionic at pH ≥ 7, cationic ($DDHA^+$) at pH ≤ 3 and a nonionic –cationic mixture between pH 3 and 7.

I.8 (c) Temperature

The temperature dependence of the CMC of surfactant in aqueous medium is generally attributed to the characteristic features of solubility-temperature relationships. The cmc value first decreases with temperature to some minimum and increases with further increase in temperature. The minimum in the curve for ionic surfactants occurs typically between 20 and 30°C. Whereas isolated examples exist of minima in cmc-temperature profile for nonionic surfactants. Such minima were observed at approximately 50°C for a series of octyl phenoxy ethoxy ethanols with oxyethylene chain lengths of between 6 and 10.[193]

The variation of CMC with temperature for ionic and nonionic surfactant is illustrated in Figure 1.9. In case of nonionic surfactants there is typically a monotonic decrease in CMC with increasing temperature. This is because the dehydration phenomenon is quite predominant with increase in temperature resulting in increase in hydrophobicity. Different factors are responsible for the effect of temperature on cmc of nonionic surfactants, viz. i) the change in water structure around the ethylene oxide units (EO), ii) change in hydrogen bonding networks and iii) changes in the conformation of EO groups.[194,195]

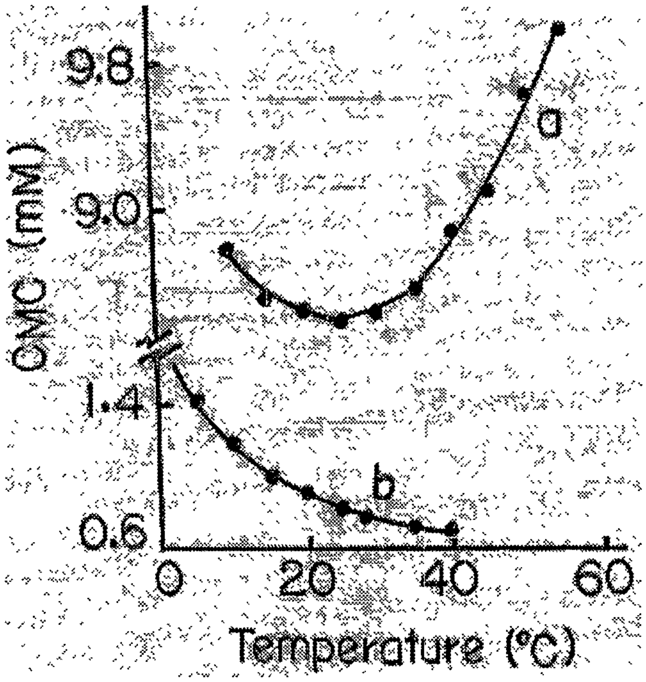


Figure I.9 Variation of CMC temperature for (a) sodium dodecyl sulphate; (b) $C_{10}E_5$ [72]

However, in ionic surfactants an altogether different behavior is observed. The CMC-temperature relationship is complex here. The CMC increase with increasing temperature after passing through a minimum at lower temperature region (Figure 1.9). This decrease in CMC at lower temperature can be ascribed to the lowering of the hydrophilicity. Further increase in the CMC with temperature is due to the disruption of water structure around the hydrophobic portion of the surfactant molecule that opposes the micellization hence higher CMC.[72] The position of minimum in cmc-temperature profile has a thermodynamic significance i.e the minimum in the cmc represents the minimum in standard free energy of micelle formation[196,197] that occurs at temperature at which $\Delta H^0_m = 0$. Experimental evidence also suggests that the temperature at which minimum in cmc is observed is at which ΔH^0_m is practically zero.[198]

For zwitterionic surfactants of type alkyl betaines, a steady decrease in the cmc is observed[199] with increase in temperature in the range (6-60°C).Zielinski et al.[200]

studied the effect of temperature (15-55°C) on micelle formation of aqueous solutions of alkyl trimethylammonium bromides having octyl, decyl, dodecyl and tetradecyl chains. The value of cmc gives minima at 47, 28, 20 and ca 15°C for the octyl, decyl, dodecyl, and tetra decyl derivatives respectively. del Rio et al.[122] evaluated the cmc of N-octyl trimethyl ammonium bromide at different pH (3.2, 7.0 and 10.0) and different temperatures (15-35°C) and they also observed a minima around 25°C at all these pHs.

In the case of gemini surfactant the variation in CMC with temperature is similar as in the case of nonionic surfactant i.e. the CMC decrease with rise in temperature The decrease in the cmc for 16-4-16 with increasing temperature may be due to enhancement of the degree of ionization, which causes a modification of the magnitude of electrostatic repulsion, as well as due to destruction of water structures surrounding alkyl chains.[201]

I.8 (d) Pressure

The effect of pressure on self-organization of surfactants has been studied.[198] The CMC-pressure plot passes through a maximum. Figure. 1.10 depicts a representative illustration of change in cmc as a function of pressure. The increase in pressure initially retards micelle formation and later on favours after a certain threshold value of pressure is reached. The increase in CMC is due to the breaking of water structure at higher pressures. The release of surfactant molecules at lower pressures and their association at higher pressures together with changed dielectric constant of the solution with applied pressure also play vital roles in the self-organization.[72]

The effect of pressure on cmc of a series of alkyl trimethyl ammonium bromides and on sodium dodecyl sulphates has been mainly studied by conductivity measurements.[202-205] Mesa[198] studied the relation between the cmcs and temperature/applied pressure using an experimental data fit and explained it in terms of thermodynamic considerations. Sugihara et al.[119] studied effect of pressure on cmc of Nonyl methyl glucamide /Sodium perfluoro octanoate surfactant mixtures.

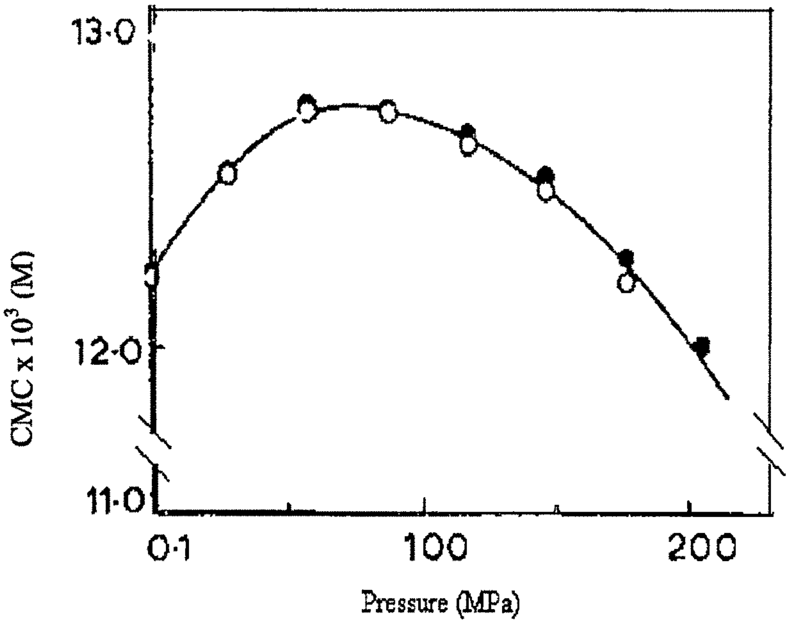


Figure I.10. CMC of dodecylpyridinium bromide as a function of pressure at 303 K; (O) optical method; (•) electroconductivity method.[205]

I.9 CMC/C_{20} RATIO[1]

It is the ratio between the CMC of particular surfactant and the concentration of the surfactant in the bulk phase that produces a reduction of 20 dyn/cm in the surface tension of the solvent. It is convenient way of measuring the relative effects of some structural or microenvironmental factor on micellization and on adsorption.

An increase in CMC/C_{20} ratio by introduction of some factors indicate that micellization is inhibited more than adsorption or adsorption facilitated more than micellization and vice versa.

It is observed for the data that (ref.1, p. 143) the CMC/C_{20} ratio

(i) Is decreased by an increase in temperature in the range of 10-40°C.

(ii) Is increased considerably by the replacement of a hydrocarbon chain by a fluorocarbon- or silicon-based chain.

(iii) Is increased by the introduction of a larger hydrophilic group.

(iv) Is increased by the introduction of branching in the hydrophobic group or positioning of the hydrophilic group in a central position in the molecule.

In the case of POE nonionics the CMC/C_{20} ratio (i) increases with increase in the number of OE units in the POE chain as constant hydrophobic chain length. (ii) increases with decrease in the length of the alkyl chain, at constant number of EO units in the POE chain. The first effect is due to the increase in the size of the hydrophilic head group with this change, the second effect may reflect the larger diameter of the micelle as the alkyl chain length is increased with resulting larger surface area to accommodate the hydrophilic head groups.

The decrease in the CMC/C_{20} ratio with increase in temperature occurs either because the size of the hydrophilic group decreases as a result of dehydration with this change or because the surface area of the micelle increases with this change. In general ionic surfactants with a single straight chain hydrophobic group in aqueous solution show low CMC/C_{20} ratios of 3 or less, while POE nonionic under the same conditions show of about 7 or more. Zwitterionics have CMC/C_{20} intermediate between those of ionic and POE nonionics. However in the presence of additives the variation is not linear (See Chapter VI, Table 1).

I.10 SOLUBILITY-TEMPERATURE RELATIONSHIP

The solubility of the surfactant is strongly temperature dependent. There are many important and intriguing temperature effects in surfactant self-assembly like Krafft temperature and cloud point.

I.10.1 Krafft point

Krafft point (T_K) is an important physical property of ionic surfactant, establishing the minimum temperature at which a surfactant can be used. The solubility of ionic surfactants in water is influenced by temperature, and the "***Krafft point***" or "***Krafft temperature***"[206] is the temperature at which a hydrated surfactant crystalline solid melts and form micelles in solution. Below this temperature, there are surfactant monomers in solution, in equilibrium with solid, but the concentration is below CMC so the solubility is limited.[207] If a micellar solution is cooled below the Krafft point, it will precipitate out of solution and detergency of the solution will be lost.[208] This temperature was the same as that required to completely dissolve the hydrated solid surfactant and it can also be judged visually to be the point of complete clarification of the surfactant system.

Krafft temperature of the surfactant is important which give information about the conditions in which a surfactant acts. This is useful to select an appropriate surfactant for a special application. Fung et. al [209] mentioned that below T_k, the surfactant concentration is not high enough to form micelles. So it is essential to perform the experiment above the T_k[209]. (please see the method used in Chapter I).

Krafft point may vary dramatically with subtle changes in surfactant chemical structure. Several aspects regarding the influence of molecular structure on the Krafft point are known. Jaladi *et al.*[208] have mentioned that for wide variety of anionic surfactants, the Krafft point increase on average 5.5°C for each methylene ($-CH_2-$) group in the hydrophobic tail. Also, for the one case available, there is an average of 9°C per ethylene oxide residue ($-CH_2-CH_2O-$) in the hydrophilic head group. However followings are some general remarks on the variation of Krafft point for alkyl chain surfactants;

(i) Krafft point increases strongly as the alkyl chain length increases. The increase is not regular but displays an odd-even effect,

(ii) Krafft point is strongly dependent on the head group and the counter ion. Salt addition raises the Krafft point, whereas many other co-solutes decrease it.

(iii) There is no general trend for the counterion dependence, e.g. in case of alkali alkanoates, the Krafft point increases as the atomic number of counterion decreases, while the opposite trend is observed for alkali sulfates. Whereas for cationic surfactants, the Krafft point is typically higher for bromides than for chlorides and is still higher for iodides. With divalent cations, the Krafft point is often much higher.

If the solubility of surfactant is low, it will not be effective and efficient in various applications i.e. higher Krafft temperature surfactants are not much useful. Hence development of surfactants with lower Krafft points is essential during the design of surfactants.

Nishikido et al[210] studied the effect of pressure on the Krafft point of ionic surfactants. The authors concluded that the Krafft temperature increased rapidly with pressure, and their model proved that Krafft temperature is a melting point of the hydrated surfactant solid. Nishikido et al[211] also observed the Krafft temperature for aqueous solution of nonionic surfactant under high pressure.

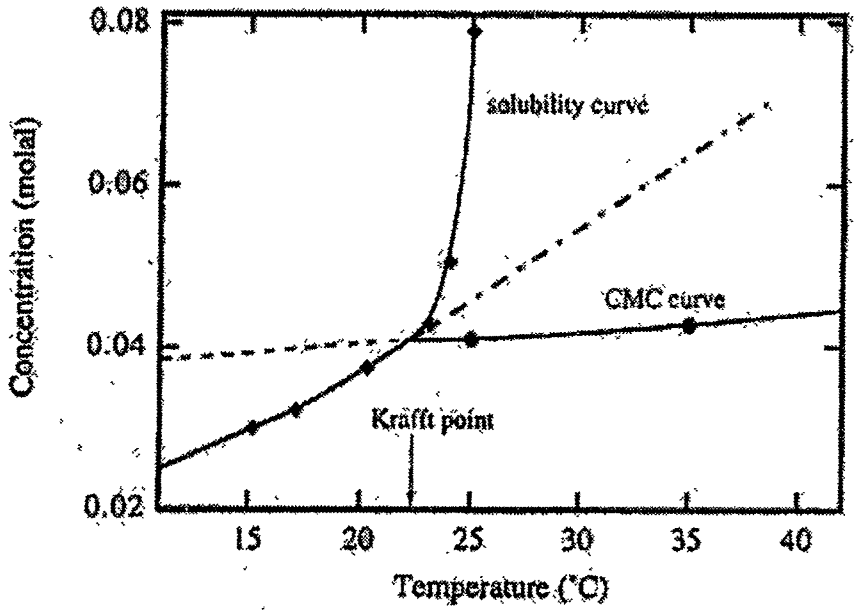


Figure I.11. Temperature dependence of surfactant solubility in the region of Krafft temperature.[107]

Zana [212] recently reported the Krafft temperature of series of 12-s-12, 16-s-16 and other cationic gemini surfactants and showed that the Krafft temperature may even be >40°C. The temperature dependence of surfactant solubility in the region of Krafft point is illustrated in Figure 1.11.

I.10.2 Cloud point

Cloud point (CP) is the characteristic feature of nonionic surfactant. A 1% (w/v) solution of a nonionic surfactant is isotropic at low temperatures and at higher temperatures a critical point is reached above which the solution becomes turbid. This temperature is referred to as the "***Cloud Point***" of the surfactant at a particular concentration. At this temperature the two phases exist, one-surfactant rich and other aqueous. The separation is believed to be due to the sharp increase in the aggregation number of the micelles leading to the formation of larger aggregates and decrease in the intermicellar interactions[213, 214] resulting from the decreased hydration of oxyethylene groups in the POE hydrophilic group with rise in temperature. Nakagawa[215] stated that this phase seperation occurs because of the difference in density of micelle-rich and micelle-poor phase.

The temperature at which clouding occurs depends upon the structure of the polyoxyethylene nonionic surfactant. For a particular hydrophobic group, the larger the percentage of OE in the surfactant molecule, the higher the CP. Although this relation between OE percentage and the CP is not linear. In general, long chain nonpolar solubilizates, such as saturated aliphatic hydrocarbon and alkyl halides, which are solubilzed in the inner core of the micelle, appear to cause an increase in the cloud point of the solution, where as polar and polarizable compounds such as fatty acids and alcohols of medium chain length, phenol etc. depress the CP.[216]

The increase in the Cp on solubilization of long-chain nonpolar material interior of the micelle may be due to the resulting increase in the radius, and hence the surface of the micelle, leaving more room at the micelle-water interface for increased hydration of the POE chains. On the other hand, the decrease in CP when polar compounds are solubilized in the outer regions may be due to decreased hydration of the POE chains as a result of competition for the hydrable sites by the polar solubilized compounds. Ions that are water structure formers (hard bases: F^-, OH^-,SO_4^{2-},Cl^- PO_4^{3-}) lower the CP of POE nonionics by decreasing the availability of nonassociated water molecules to hydrate the ether oxygens of the POE chain. While Ions that are water structure breakers (e.g. larger polarizable anions; soft base: SCN^-,I^-) increase the CP by making more water molecules available to interact with the POE chain.[217] Kabir-ud-din et al. also reported the CP of ionic surfactant, SDS in presence of quaternary ammonium ions.[218-220a]

Determination of Cloud point with time is a way to monitor the auto oxidation of POE surfactant.[220 b] Recent investigations have revealed that the dermatological effect seen with alcohol ethoxylates may not be caused by intact surfactant but by oxidation products formed during storage. Very recently Holmberg *et al.*[220 b] studied the oxidative degradation of nonionic surfactants when exposed to air.

They observed the cloud points of 1% aqueous solutions of $C_{12}E_6$ and $C_{12}E_5$ dropped from 60 to 31°C and from 32 to 15°C, respectively, on standing in closed bottles at 40°C fro 170 days.

The cloud point used in the physicochemical characterization was measured at ~1 wt% surfactant in water. This is the standard way of surfactant manufactures to describe this property. However it is well known that the phase separation, i.e. the cloud point of a nonionic surfactants is concentration dependent phenomena. Ksohy *et al.*[220c]observed the CP of Triton X 100 and Triton X 114 a s a function of concentration from 1 to 10%. They observed a minimum ~3% in the case of TX 100. However in case of TX 114 the CP remain more or less constant at low concentration, while increases monotonously from ~3%. Similar results were obtained by Heusch[220d]. In the present work we studied the phase separation of $C_{12}E_9$ and $C_{12}E_{10}$ nonionic surfactant as shown in Chapter VII and IV b respectively. The decrease in CP with increase in concentration is due to the increase in micelle concentration. However at higher concentration the CP increases which due to formation of structured water-surfactant system.[220c]

I.11 METHODS TO INVESTIGATE THE MICELLAR SOLUTIONS

I.11.1 Macroscopic Techniques

The macroscopic techniques such as surface tension, conductivity, Krafft temperature, cloud point and viscosity are widely used to investigate the micellar solutions.[221] These techniques are very useful for the observation of transitions, as an abrupt variations of macroscopic properties reveals some changes in microstructure. For example, CMC can be measured by several different macroscopic techniques.[108] The transition from spherical to rod-like micelles is accompanied by significant increase in viscosity.[222-224]

I.11.2 Scattering Techniques

The scattering techniques are the most direct techniques for the study of the structures of micellar solutions. A scattering technique measures the scattered intensity I as function of wave vector transfer Q ($=4\pi \mathrm{Sin}\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident radiations). Small-angle neutron scattering (SANS), small-angle x-ray scattering (SAXS) and light scattering (LS) are widely used. Light scattering technique includes both static light scattering and dynamic light scattering (DLS). In DLS, one measures the time correlations of the fluctuating intensity of light scattered from a system of colloidal particles undergoing Brownian motions. The scattering techniques are used not only to investigate the micellar structures but also for understanding the inter and intra micellar interactions. Several reviews on the principles, methods and limitations of scattering methods applied to micellar solutions are available.[225-230] SANS, SAXS and DLS are the complementary techniques for the study of micellar solution on a similar length scale of ~100 Å. For the structural study of micellar solutions, the use of SANS over SAXS is generally preferred as it is possible to obtain a very good contrast between the micelles and the solvent by preparing the solution in D_2O instead of H_2O. DLS is used to determine the hydrodynamic properties of micellar solutions. The hydrodynamic radius (R_h) of the micelle is obtained by measuring the self-diffusion coefficient in the dilute limit, where the concentration between the micelles can be neglected.[231] In an ionic micelles, it is difficult to get a noninteracting limit even at low concentration of surfactant molecules. Therefore measurement of R_h by this technique is subject to unknown errors. SANS is used in both the dilute and concentrated micellar solutions (see section 1.11.2.1).

I.11.2.1 Small-angle neutron scattering (SANS)

Thermal neutrons are known to be ideal probe for investigating the structure and dynamics of materials at microscopic level.[232,233] Neutrons are now routinely used by solid-state physicists, chemists, biologist and metallurgists. Neutron scattering consists of a whole family of techniques and small-angle neutron scattering (SANS) is one of these.[234]

SANS is an ideal technique to study the micellar morphology[235,236] and this has been also demonstrated for surfactant micelle in presence of various additives.[237-239] The techniques of SANS is used for studying the structure of a material on length scale of 10-1000Å. This covers the length scale of particular interest to a number of applied problems relating to polymer, ceramics and biological systems. In particular, SANS is used to study the shape and sizes of the particles dispersed in homogeneous medium. In suitable case, SANS also provides information about interparticle interactions.

SANS is a diffraction technique, which involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The wave vector transfer Q ($=4\pi \mathrm{Sin}\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident neutrons) in these experiments are small, typically in the range of 0.02 $Å^{-1}$ to 0.32 $Å^{-1}$. The wavelength of neutrons used for these experiments usually are between 4 and 10 Å. Since the small Q values occur at small scattering angles, the technique is therefore called small-angle neutron scattering.

I.11.2.2 SANS Spectrometer

SANS is a diffraction experiment, which involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle (Figure 1.12). The typical Q range in SANS experiments used is 0.02 to 1 $Å^{-1}$. To obtain such low Q values SANS instruments use larger wavelength and small scattering angles. A SANS instrument mainly consists of three parts: (i) monochromator (ii) collimatior and (iii) detector. The monochromator consists of a polycrystalline BeO fiter, which has a Bragg cut-off at 4.7 Å. The neutrons from the reactor are allowed to pass through this filter, which give a monochromatic beam of neutrons. The BeO filter is kept at liquid-nitrogen temperature. The collimation system between the monochromator and the sample consists of two rectangular slits separated by a distance of 2m. This colliminator gives an angular divergence of ±0.5° of the incident beam. The measured incident neutron flux at the sample position is 2.2 x 10^5 n/cm^2/s. The scattered neutrons from the sample are detected using a 100 cm long, 3.8 cm dia He^3 linear position sensitive detector (PSD) The distance between the sample and the detector is 1.8 m. Data from the PSD are stored in a multichannel analyzer as intensity vs channel number. The resolution function of the diffractometer has been calculated using Monte Carlo simulations.[240]

SANS experiments were carried out on the micellar solutions prepared by dissolving known amount of surfactant in D_2O. The use of D_2O instead of water for preparing solution for SANS experiments was because this provides a very good contrast between the micelles and the solvent. SANS experiments were performed on the SANS instrument at the DHRUVA reactor, Trombay, BARC, Mumbai, India.[240] The instrument makes use of a BeO filter to obtain a monochromatic beam. The mean wavelength of the incident neutron beam λ is 5.2 Å with a wavelength resolution ($\Delta\lambda/\lambda$) of approximately 15%. The scattered neutrons are detected in an angular range of 0.5-15° using one-dimensional linear position sensitive detector (PSD). The accessible wave vector transfer, Q ($=4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident neutrons) in above instrument is 0.018 $Å^{-1}$ to 0.30 $Å^{-1}$. PSD allows simultaneous recording of the data over the full Q range. The solutions were held in a 0.5 cm path length UV-grade quartz cell with tight fitting teflon stoppers. Experimental measuring times were between 180-200 min. The SANS data were recorded at 30, 45 and 60°C (±0.2°). At a given temperature, the concentrations of the surfactant and additives were varied. In all the data, scattering intensities were corrected for the background and the solvent scattering and normalized to absolute cross-section units. Thus a plot of cross section per unit volume ($\partial\Sigma/\partial\Omega$) vs scattering vector (Q) were obtained.

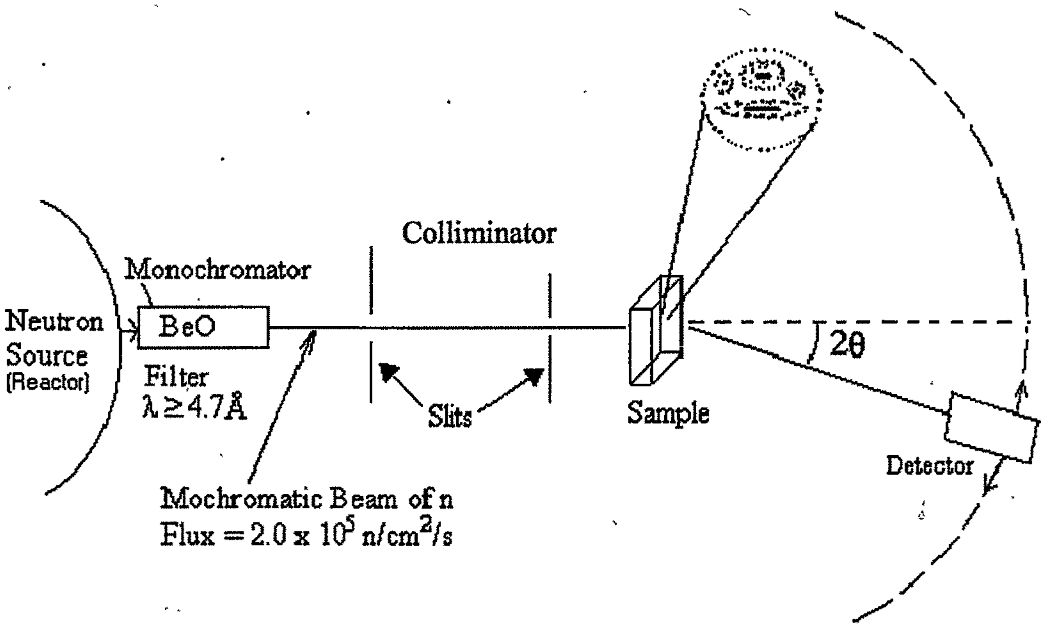


Figure I.12 Schematic of SANS diffractometer [240]

The sample to detector distance was 1.8m for all runs. The intensities then were normalized to absolute cross-section units. Thus, plot of cross section per unit volume ($\partial\Sigma/\partial\Omega$) vs scattering vector (Q) were obtained. The uncertainty in the measured scattering intensities is estimated to be 5%. A Schematic of SANS diffractometer is given in Figure 1.12.

Although, in many ways SANS is similar to the well known SAXS technique,[241] it has following unique features that distinguish it from SAXS and is used with great advantages in the study of micellar solutions.

(i) The measuring of the absolute scattering cross-section is relatively easy.

(ii) The possibility of varying the scattering length density of the solvent continuously and by a large amount by simply changing the D_2O/H_2O ratio of the solvent. In the case of micellar solutions, the isotope effect is absent.[242] This way one can enhance the contrast between the micelle and the solvent in an experiment.

(iii) The possibility of a selective deterioration of a particular functional group in a surfactant molecule to enhance the signal from the selected functional group.

For SAXS the contrast variation technique is rather difficult to apply without changing the solvent chemistry drastically. Since aggregate formation results from a delicate balance between the hydrophobic interaction and the charge repulsion on the surface of the micelle, a small change in solution condition can induce a large change in the state of an aggregate. In general SAXS technique is not used for the determination of the structure of the micelles because there is no contrast between the solvent and the hydrocarbon part of the micelle. X rays are primarily scattered by the polar parts of the surfactant molecules. However, the SAXS can be used to study the structure of the head group region and also the counterions distribution.[243]

SANS study is discussed in Chapter III and Chapter VI where the aggregate structure of $C_{12}E_{10}$–sugars and $C_{12}E_9$-amino acids complex systems respectively were investigated. (Details regarding SANS data analysis, SANS data correction, and calculation of various SANS parameters like shape, size and aggregation are given in Chapter VII).

I.11.2.3 Dynamic light scattering (DLS)

The normalized time correlation function of the scattered intensity, $g^{(2)}(\tau)$ can be written as[244]

$$g^{(2)}(\tau)=\frac{\langle I(0)I(\tau)\rangle}{\langle I\rangle^2} \tag{1}$$

For a suspension of monodisperse, rigid, spherical particles undergoing Brownian diffusion, the correlation function decays exponentially and is given as

$$g^{(2)}(\tau) = \exp(-Dq^2\tau) \qquad (2)$$

where D is the translation diffusion coefficient and q is the magnitude of the scattering wave vector given by q = $(4\pi n/\lambda)$ sin $(\theta/2)$. Where n is the refractive index of solvent (1.34 for the water at 25°C). Transitional diffusion coefficient values thus obtained were used to calculate the dissociated hydrodynamic radius of the micelle by applying well known Stokes-Einstein equation

$$R_h = \frac{kT}{6\pi\eta_o D_0} \qquad (3)$$

where kT is the thermal energy factor and η_o is the solvent viscosity. This technique we used both in the mixed surfactant system (Surfactant in presence of another surfactant as additive) as well as in the presence of nonsurfactant additives on nonionic surfactants (see chapter II and VI).

I.11.3 Spectroscopic Techniques

The formation of micelles will influence the local molecular interactions for the components. This in turn shows up a change in a number of spectroscopic parameters. Thus it is possible to probe several different aspect of the molecular organization in micellar solution by spectroscopic techniques such as, fluorescence quenching and nuclear magnetic resonance (NMR). Fluorescence is an ideal technique to determine the micellar aggregation number (N_{agg}) of surfactant solution[245] (see chapter II A and II B). The ratio of intensity of first (I_1) and third (I_3) vibronic peaks i.e. I_1/I_3 of the pyrene fluorescence emission spectrum in presence of surfactants is considered to be the index of micropolarity of the system i.e. it gives an idea of microenvironment in the micelle. A low value of this ratio (< 1) is generally taken as the pyrene having nonpolar surroundings whereas higher value (> 1) is taken as the pyrene having polar surroundings.[246]

Another general technique for the study of micellar solutions is nuclear magnetic resonance (NMR).[247,248] With the advent of Fourier transform techniques as well as high field superconducting magnets, NMR studies are feasible at submillimolar concentration for many nuclei and thus highly appropriate for investigations of micelle formation. This technique has highest spatial resolution. This obvious advantage has some drawbacks: Detail information such as particle size is difficult to extract from such information.

I.12 PERFORMANCE PROPERTIES OF SURFACTANTS

Almost in all industrial applications; a combination of surface-active properties is usually preferred. The interfacial and solution behaviour of surfactants gives various surface-active properties; *viz.* i) emulsification/demulsification, ii) wetting, iii) foaming/ defoaming, iv) detergency v) viscosity, and vi) solubilization.[249]

Viscosity of surfactants is useful in handling of liquids in processing and also to the formulation of end use products in which a desired physical form is required. In formulated products, the viscosity of surfactants in aqueous medium may be affected by the presence of electrolytes or other foreign substances that modify the water structure. Some reports are there in literature on the viscosity of pure surfactant solution with or without electrolyte. [250,251] The viscosity of surfactant solution arises because of the interaction of both the hydrophobic core and hydrophilic outer shell of the micelle with water. It measures the solute-solvent interaction as well as the shape and size of the micelle. The latter are effected by temperature changes.

Many authors [252,253] have discussed the effect of inorganic salts on ionic surfactants in terms of electrostatic interactions and changes in water structure. Kabir-ud-Din[254] *et al.* extensively reported their observation on the structural changes in micellar systems by alcohols, amines and aromatic hydrocarbons.

The effect of electrostatic charge on the viscous flow has been investigated as the electroviscous effect.[255] Also aggregation number, volume of the hydrocarbon core, oxyethylene layer of the micelle have been calculated using intrinsic viscosity, as viscosity is depends on micelles, micelle solvent and micelle-micelle interaction.[256,257] The relationship between the structure of the micelles and its viscosity was correlated to the sharp increase in the viscosity of concentrated surfactant solution to the formation of rod like micelle that form network in solution.

Changes in the viscosity of aueous solutions of nonionic surfactant in presences of additives has been investigated.[258] Rhodes *et al.*[259] have reported the effect of oxyethylene chain length on the viscosity. We studied the viscosity of different surfactant systems in the absence and presence of different additives like sugars, alcohols and amino acids (see Chapters V, VI, and VII respectively).

Foam is produced when air or some other gas is entrapped beneath the surface of liquids that expends to enclose the gas with a film or liquid. Foaming is a property inherent to all surfactant solutions.

The theoretical basis of foam has been extensively studied and its physicochemical principles are well addressed.[260] Anionic surfactants are good foamers as nonionic are poorfoamers.[261]

The foaming power of detergents solution and its stability shows significant variations with respect to presence of, i) additives, ii) chemical structure, iii) surfactant concentration and iv) temperature. Electrolytes generally destabilize the foam by screening the repulsive forces between the ionic head groups that leads to reduce repulsion between surfactant layers or opposing film interface which in turn lead to faster film drainage. POE nonionic surfactants generally produce less and much less stable foam than ionic surfactants in aqueous media. These effects are due to large surface area per molecules and the absence of highly charged surface film in these foam. (1) In POE nonionics both foam stability and foam volume reach a maximum at a particular OE chain length.[262] The foam of POE nonionics decreases markely at or above their cloud points. Detergency is a complex process involving interactions between surfactants, soil, textile and surface. The choice of surfactant is the key to success of the process. POE nonionics are more efficient in soil removal and prevent their redeposition than ionics. This is due to their low CMCs and due to greater surface coverage per molecules when adsorbed on substrate and soil. Increasing the length of hydrophobic groups the efficiency of oily soil removing by decreasing the CMC and vice versa.

I.13 THERMODYNAMICS OF MICELLIZATION [263]

All physico-chemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principle and the laws of thermodynamics can be applied to get the information regarding free energy, enthalpy and entropy of micellization.

There are two main approaches to the thermodynamic analysis of micellization process, i) the mass action model and ii). phase separation model. Generally, the approaches that is selected depends on the complexity of the system, properties to be described and the desired level of detail.

I.13.a Mass action model

In this model, the micelle and monomeric species are considered to be in association-dissociation equilibrium and law of mass action can be applied. According to this model the micellization is considered as a stepwise process and the micelles are not monodisperse, but there is a distribution of aggregation numbers of micelles or micelles are polydisperse. In application of mass-action model, it is essential to know every association constant over the whole stepwise association from monomer to micelle, which is almost impossible experimentally. Therefore this model has limitation in that it considers only one species of micelle, i.e. it assumed monodispersity of micelle size. This model was originally applied mainly to ionic surfactants but later on Corkill et al.[264] applied it to nonionic surfactants too.

According to this principle, above CMC, the concentrations of monomer and micelle are interdependent. Increase of monomer concentration increases miceller concentration and vice-versa in accordance with the following equilibrium

$$n\,(S^- \text{ or } S^+ \text{ or } S) \xrightleftharpoons{K_M} (S_n^- \text{or } S_n^+ \text{or } S_n) \qquad (4)$$

where S^- or S^+ or S = micelle; n=aggregation number, and K_M =micellezation constant with free energy of micellization $\Delta G_M^o = RT \ln K_M$.At CMC, by conceptual approximation, the free energy of micellization expressed per mole of monomer unit ($\Delta G_m^o = \Delta G_M^o / n$) is given by the relation,

$$\Delta G_m^o = RT \ln CMC \qquad (5)$$

Considering counter-ion binding to ionic micelles, eqn (2) is modified to

$$\Delta G_m^o = (1+f) RT \ln CMC \qquad (6)$$

where f = fraction of counter-ion bound to a micelle,

For nonionic surfactants, f=0 and eqn (6) is reduced to eqn (5).

ΔG_m° is the measure of the standard free energy change for the transfer of one mole of surfactant from solution to micellar phase.

I.13.b Phase Separation Model[263]

This model considers micelle as a separate phase. The monomer concentration at and above CMC remains nonvariant; with increasing surfactant concentration above CMC micelles are only formed. This is like solubility of a substance where above the solubility limit excess amount separates out as the insoluble phase. The micellar pseudophase on the other hand remains in solution. Based on the phase equilibrium,

$$\text{monomer} \rightleftharpoons \text{micelle} \qquad (7)$$

at a constant temperature, chemical potential of surfactant monomer in solution (μ_m) is equal to the chemical potential of the monomer in the pseudomicellar phase (μ_M) thus,

$$\mu_m \rightleftharpoons \mu_M \tag{8}$$

Explicitly,

$$\mu_m^o + RT\ln a_m = \mu_M^o + RT\ln a_M \tag{9}$$

Wherefrom we again get

$$\Delta G_m^o = RT\ln CMC \tag{10}$$

for nonionic micelle, and

$$\Delta G_m^o = (1+f)RT\ln CMC \tag{11}$$

for ionic micelle. The μ_m^o and μ_M^o are the standard chemical potentials of monomer and micelle respectively and a_m and a_M are their corresponding activities (a_M=1, for micellar pseudophase is taken to be pure phase). It is noted that in the above thermodynamic treatments, at the CMC, the equilibrium concentration of free monomer is considered equivalent to CMC.

The equations for the free energy of micellization by phase seperation and mass action model are similar, but the two equations differ slightly because of differences in the way in which the mole fractions are calculated. In phase seperation model, the total number of moles present at cmc is equal to the sum of the number of moles of water and surfactants, whereas the total number of moles in the mass action model is equal to the moles of water, surfactant ions, micelles and free counterions. Unfortunately, the interpretation of mixed micellization based on mass action model have not agreed well with the experimental CMC values, possibly due to the difference in the physico-chemical properties of mixed micelles from those of micelles of individual components. Due to the number of parameters required and the complexity of mass action model compared to phase seperation model, the former has only been applied in modeling a few systems.

The numerical values of ΔG_m° differ because the mole fractions are calculated differently. In the phase-separation approach the total number of moles is that of water plus monomer. In the mass-action approach micelles and free counterions are also included. At CMC the two totals are approximately equal, and both models yield similar results.[265]

The corresponding entropy of micellization (ΔS_m°) and standard enthalpy (ΔH_m°) per mole of the monomer can be computed from the slope and intercept respectively of linear ΔG_m° vs Temperature plots or also by using the following well known thermodynamic relations,

$$\Delta H_m^\circ = -RT^2 \frac{d \ln CMC}{dT} \tag{12}$$

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \tag{13}$$

The enthalpy change represents the net change in intermolecular forces upon micelle formation .The entropy change includes change in the degrees of freedom of both solvent and surfactant molecules.

In the computation of ΔG_m° for ionic surfactants, apart from the transfer of surfactant molecules from aqueous phase to micellar phase; the transfer of $(2-\alpha)$ moles of counter-ions is also to be considered and hence ΔG_m° of ionic surfactant is defined as,

$$\Delta G_m^\circ = (2-\alpha)RT \ln X_{cmc} \tag{14}$$

where α is the degree of ionization of micelle; and is often computed from the ratio of the slopes of post micellar region to that of premicellization region of conductance – concentration profile.[266] The relation given in eqn 6 and 11 are same to eqn 14. The fraction of counterion bound to micelle $'f' = 1-\alpha$, where $'\alpha'$ is the degree of ionization of the micelle.

I.14 ADSORPTION AT INTERFACES

Surfactant molecules tend to accumulate at air/water or oil/water interfaces. The surface of a liquid is a boundary between two bulk phases namely liquid and air. The ability of surfactants to adsorb at interfaces and lower the interfacial energies as well as their ability to form aggregates in water are the most important properties of surfactants. Surfactant adsorption plays a critical role in many important industrial applications of surfactants such as wetting, adhesion, flotation, dispersion stability, detergency and thin-film formation. Thus the knowledge of surface area occupied by surfactant at an air/water interface is very important in surface science in order to optimize the conditions as per desired application. The variation of surface tension (γ) with composition in case of solutions is one of the most important routes to obtain information about surface concentration.

J. W. Gibbs derived a relationship rooted in thermodynamics and well known as Gibbs adsorption isotherm,[267] in 1878. The Gibbs equation expresses the equilibrium between the surfactant molecules at the surface or interface and those in the bulk solution. It is very useful as it provides a means by which the amount of surfactant adsorbed per unit area of the surface, "Surface Excess" may be calculated.

The most general form of Gibbs equation is written as,

$$d\gamma = -\sum \Gamma_i d\mu_i \qquad (15)$$

where $d\gamma$ is the change in surface or interfacial tension of the solvent; Γ_I is the surface excess concentration of the Ith component i.e it is the excess per unit area of surface of the Ith component present in the system over that present in a hypothetical system of same volume in which the bulk concentration in two phases remains constant up to an imaginary dividing surface; $d\mu_I$ is the change in chemical potential of the Ith component of the system.

For a two component system at constant temperature,

$$d\gamma = - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{16}$$

where subscripts 1 & 2 refer to solvent and solute respectively. Assuming Γ_1 – the excess concentration of the solvent to be equal to zero and for dilute solution,

$$\Gamma_2 = \frac{-1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right) \tag{17}$$

$$= \frac{-C}{2.303nRT}\left(\frac{d\gamma}{dC}\right) \tag{18}$$

where C is the concentration of surfactant. Above equation is applicable to the adsorption of non-dissociating solutes such as nonionic surfactants.

For solutions containing a single surfactant, 'n' is the number of species whose interfacial concentration changes with change in the bulk phase concentration of the surfactant and thus the coefficient 'n' is equal to 1 in the case of nonionic surfactants.

For ionic surfactants, in absence of any added electrolyte,

$$\Gamma_2 = \frac{-1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right) \text{ mol cm}^{-2} \tag{19}$$

where 'γ' is in dyne/cm, concentration of surfactant in molarity, R in ergs mol^{-1} K^{-1} and the coefficient 'n' is equal to 2. The $d\gamma/d\log C$ is obtained from the surface tension-log$_{10}$Concentration plot.

From the surface excess, the minimum area per molecule ($A_{\text{min.}}$) of the surfactant at the air/water interface can be computed which provides the information on the degree of packing and the orientation of the adsorbed surfactant molecules. The minimum area per molecule of the surfactant at the air/water interface is computed as,

$$A_{\text{min.}} = \frac{10^{14}}{N_A \Gamma} \text{nm}^2 \tag{20}$$

where N_A is Avogadro number and Γ is surface excess concentration in mol cm^{-2}.

The surface excess concentration under the conditions of surface saturation Γ_m is generally used as a measure of the maximum extent of surfactant adsorption. There are several factors, which determine the maximum amount of surfactant adsorbed (Γ_m) at the air/water interface. Γ_m depends on surfactant structure, presence of electrolyte and temperature. Rosen[1] has tabulated values of Γ_m for a wide variety of anionic, cationic, nonionic and zwitterionic surfactants. The length of the hydrophobic group has almost no effect on Γ_m except when it exceeds 16 carbon atoms; a significant decrease in Γ_m is observed, due to coiling of the chain. For poly oxyethylene nonionic surfactants of fixed oxyethylene chain length, the value of Γ_m remains almost unchanged with the length of hydrocarbon chain length.

The most pronounced effect of structure on Γ_m comes from the nature of the hydrophilic group or the size of the head group. Surface concentration decreases as the size of the head group of surfactant increases. Presence of electrolyte has a no effect on Γ_m. Increase in temperature, decreases Γ_m for ionic surfactants, whereas Γ_m increases with increase in temperature for nonionic surfactants.[72] Rosen et al.[137] have reported a decrease in surface excess concentration as the temperature as well as oxyethylene chain length of nonionic surfactant increases. However, the minimum area per molecule increases with increase in temperature due to increased thermal agitation of the molecules in the surface film.

I.15 THERMODYNAMICS OF ADSORPTION

Thermodynamic investigations of adsorption of surfactants can provide two important information about the adsorbed films i.e the Gibbs free energy of adsorption as a measure of surface activity of the surfactant and the enthalpy of adsorption of surface active homologues from aqueous solution at the air/water interface.[268]

The standard free energy of adsorption, ΔG_{ad}° is defined by the relation [1,269]

$$\Delta G_{ad}^{\circ} = RT\ln_{cmc} - N\Pi_{cmc}A_{cmc} \qquad (21)$$

by considering the standard state as a hypothetical monolayer at its minimum area per molecule at zero surface pressure. The second term in above equation represents the surface work involved in going from zero surface pressure to the surface pressure at cmc (Π_{cmc}) at a constant minimum surface area per molecule ($=A_{cmc}$). When Π_{cmc} is in mNm^{-1}, A_{cmc} in nm^2, CMC in mole fraction and R is in J $mol^{-1}K^{-1}$, with ΔG_{ad}° in $kJmol^{-1}$ above equation becomes

$$\Delta G_{ad}^{\circ} = 0.001RT\ln cmc - 6.023x10^{-1}\Pi_{cmc}A_{cmc} \qquad (22)$$

The corresponding enthalpy (ΔH_{ad}°) and entropy of adsorption (ΔS_{ad}°) are computed from the well known thermodynamic relations. The standard free energy change upon adsorption determines the spontaneity of adsorption process as well as the magnitude of driving force. The standard enthalpy change for adsorption indicates whether bound making or bond breaking phenomenon during adsorption. The extent of randomness is given by the standard entropy changes during adsorption.

Motomura et al.[270] investigated the thermodynamics of adsorption of surfactants at interfaces. Sulthana et al.[185-188] extensively studied the interfacial and thermodynamic properties of anionic, nonionic and anionic/nonionic surfactant mixture in absence as well as presence of different additives.

I.16 MIXED SURFACTANT SYSTEMS

I.16.1 Binary Mixed surfactant Systems

Mixed surfactant systems form a part of surfactant formulation in nearly all areas of their application. Mixed micelles can have different sources of origin. Often it could be because of natural polydispersity of the commercial surfactants or due to the presence of impurities getting associated in the course of manufacture. Mixtures of surfactants often show better physico-chemical properties than single pure surfactants.[271-273] Mixed micellar system could also arise due to the deliberate mixing of different surfactant types to exploit synergistic behaviour in mixed systems or to have multiple qualities belonging to individual components in one mixture. Although, incorporation of solubilizates into surfactant micelle also results in the formation of micelles, generally the term mixed micelle is used to represent a micelle that is composed of surfactants that are themselves capable of forming micelle. Because of this, there has been considerable research on the molecular interactions between different surfactants in their binary mixtures, particularly in relation to the existence of 'synergy' (a condition when properties of mixtures are better than the individual components, when surfactants are purposely mixed) between them.

Like single surfactants, mixed surfactants also micellize after a critical micelle concentration. The tendency to aggregate is guided by their synergistic (attractive) and antagonistic (repulsive) inter-actions and thus is reflected in their CMC values compared to those of their components. Mixing of dissimilar surfactants often leads to synergistic behaviour due to the non-ideal interaction of the components and this results in substantially lower CMCs and interfacial tensions than the individual systems. This has lead to both theoretical and practical interest in the understanding of the behaviour of mixed surfactant systems so that they could be exploited in such fields as detergency, enhanced oil recovery etc. Mixed micellar systems involving a wide range of surfactant types have been studied and these include combinations of nonionic, anionic, cationic and zwitteronic or even gemini systems. Although anionic and cationic surfactants may from insoluble ion pairs at nearly equal molar ratios, they generally get solubilized if the proportion of one of them is considerably larger than the other.

I.16.2 Molecular Interaction in the Mixture of two surfactants

The two fundamental properties of surfactants are monolayer formation at interface and micelle formation in solution. The characteristic phenomena of surfactant mixtures are mixed monolayer formation at interface and mixed micelle formation in solution.

Many researchers have published books with a collection of review works in the field of mixed surfactant systems like Scamehorn,[273] Rubingh and Holland[274] Rakshit and Palepu[275] and Ogino and Abe.[276] These books pertain to intermolecular interaction between the hydrophilic and hydrophobic groups in addition to their applications.

During the formation of mixed micelles, both ideal and non-ideal mixing can occur. Since the hydrophobic effect, which drives the aggregation process, is not specific to surfactant head group, the formation of randomly mixed surfactant aggregates will be favored and this leads to the ideal components of mixing. But in the case of mixture comprising of different surfactants, the electrostatic repulsion between the head groups lead to non-ideal mixing in the micelle and can be treated *via* regular solution theory. This has been successfully applied in predicting the nonideal behavior of a wide variety of binary surfactant mixtures. These two theories are follows.

I.16.2.a Ideal Mixing Theory

Clint[277] has proposed ideal mixing theory by a phase seperation model to describe the phenomenon of mixed micelle formation. This model treats the micelles as a separate phase from that of dissolved surfactant unimers and proposed that the mixed micelle is an ideal solution of two surfactants. It predicts the mixture cmc, micelle composition, and unimer concentration.

The cmc values for the mixed surfactant system (c_{12}) can be calculated theoretically using the Clint's equation[278]

$$\frac{1}{c_{12}} = \frac{\alpha_1}{c_1} + \frac{1-\alpha_1}{c_2} \tag{23}$$

where c_{12}, c_1 and c_2 are the cmc values of the mixture, surfactant 1 and surfactant 2 respectively. α_1 is the mole fraction of surfactant 1 and α_2 (i.e $1-\alpha_1$) is the mole fraction of surfactant 2 in solution respectively. Although it provides the description of nearly ideal mixing, it fails to predict either the cmc or monomer concentrations of surfactant mixtures differing in head groups, where nonideal mixing is more common.

I.16.2.b Nonideal Mixing Theory

When the two surfactants forming the mixed micelle have different head group, the CMC cannot be predicated by ideal theory. Rubingh[279] has predicted the CMC of mixed micelle using regular solution theory. This approach provides a way to ideal enthalipic as well as entropic factors on mixed micelle formation. Comparison of the prediction of the theory with experimental data revels that the nonideal mixed micelle theory provides much better description than the ideal mixing theory.

This observation regarding interaction among surfactants monomer is quantified in terms of interaction parameters (β^m) Accordingly, when

(i) $\beta^m = 0$, the two surfactants form an ideal mixture,

(ii) β^m = negative, the interactions to be strongly attractive and mixed micelles are stabilized electro statically.

(iii)β^m = positive, indicate non-compatibility of constituent surfactant species and is thus a measure of antagonistic behaviour of surfactant mixture.

According to this theory, the molecular interactions between two surfactants in micelles or at an interface are commonly measured by the so-called β parameters, which are conveniently obtained from critical micelle concentration data or from surface (or interfacial tension). The micellar interaction parameter is obtained by use of following equations[1]

$$\frac{(X_1^M)^2 \ln\left({\alpha_1 C_{12}^M} / {X_1^M C_1^M} \right)}{(1-X_1^M)^2 \ln {(1-\alpha_2) C_{12}^M} / {(1-X_1^M) C_2^M}} = 1 \qquad (24)$$

$$\beta^M = \ln \frac{\left({\alpha_1 C_{12}^M} / {X_1^M C_1^M} \right)}{(1-X_1^M)^2} \qquad (25)$$

where X_1 is the mole fraction of surfactant 1 in the total surfactant in the mixed micelle and C_1^M, C_2^M and C_{12}^M are the critical micelle concentrations (cmcs) for surfactant 1, surfactant 2 and their mixture respectively at the solution mole fraction α_1. Equation 24 is solved iteratively using a computer programme for X_1, which is then substituted in to Eq. 25 to evaluate β^m.

Similarly the interaction parameter at the air/water interface is given by the relations,

$$\frac{(X_1)^2 \ln\left({\alpha_1 C_{12}} / {X_1 C_1^0} \right)}{(1-X_1)^2 \ln {(1-\alpha_1) C_{12}} / {(1-X_1) C_2^0}} = 1 \qquad (26)$$

$$\beta^{\sigma} = \ln \frac{\left(\alpha_1 C_{12} \middle/ X_1 C_1^0 \right)}{(1 - X_1)^2} \tag{27}$$

where X_1 is the mole fraction of surfactant 1 in the total mixed monolayer (on a surfactant only basis); C_1^0, C_2^0 & C_{12} are the molar concentrations in the solution phase of surfactant 1, surfactant 2 and their binary mixture respectively at a mole fraction α_1 of surfactant 1 in solution required to produce a given surface tension, γ value (obtained from γ-$\log_{10}C$ plots). In this case also Equation 26 is solved iteratively for X_1, which thus obtained is then substituted in Equation 27 to evaluate β^{σ}. β^{σ} & β^{M} are quantitatively different but qualitatively similar.

I.16.3 Synergism or Negative Synergism

The efficiency of surface tension reduction by a surfactant has been defined as the solution phase surfactant concentration required to produce a given surface tension (reduction). Synergism in this respect is present in an aqueous system containing two surfactants when a given surface tension can be attained at a total mixed surfactant concentration lower than that required of either surfactant itself. Negative synergism is present when it is attained as a higher mixed surfactant concentration than that required of either surfactant by itself.

Synergism in this respect is present when the CMC in aqueous medium of any mixture of two surfactants is smaller than that of either of individual surfactants. Negative synergism is present when CMC of the mixture is larger than the CMC of either surfactant of the mixture. Figure 1.13 illustrated both Synergism and negative synergism.

According to Rubingh's approach,[279] the micellar interaction parameter β^{M} should be constant over an entire range of composition. Such behaviour has been found to be valid in the case of anionic/nonionic surfactant mixtures of NaOL/$C_{10}(EO)_6$ and SDS/C_9PhE_{10}.[280] Rubingh's regular solution theory is useful due to its simplicity and application to other phenomena. This non-ideal solution treatment has been used to many researchers all over the world for analysis of binary surfactant mixtures[108, 207-212]

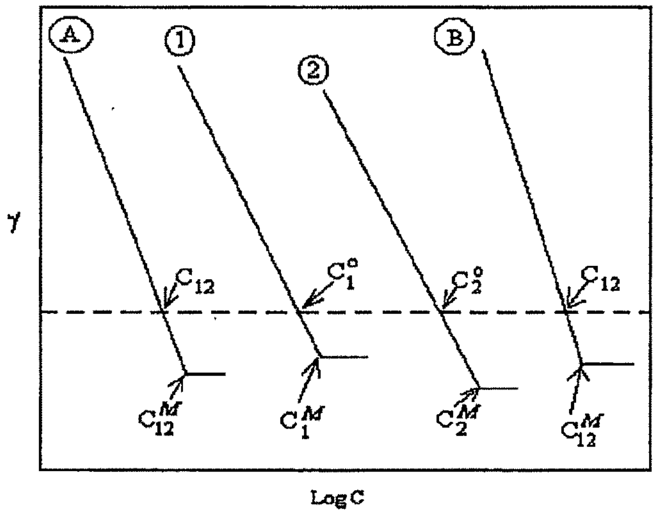


Figure I.13 Synergism or negative synergism in surface tension reduction efficiency or in mixed micelle formation. (1) Pure surfactant 1; (2) pure surfactant 2; (A) mixture of surfactant 1 and 2 at a given mole fraction α in the aqueous phase showing synergism ($C_{12} < C_1^o, C_2^o$ *or* $C_{12}^M < C_1^M, C_2^M$), (B) mixture of surfactant 1 and 2 at a given mole fraction α in the solution phase showing negative synergism ($C_{12} > C_1^o, C_2^o$ *or* $C_{12}^M > C_1^M, C_2^M$). (Ref. 1, p. 401)

Although Rubingh's treatment has been extensively used, it has a few drawbacks,

I) the interaction parameter β^M is considered to be independent of temperature and micellar composition but it has been found to be substantially temperature and composition dependent.[213]

II) Meaningful values of β^M have not been realized for some anionic/cationic surfactant mixtures. Contrary to expectations, positive β^M values have been obtained at all mole fractions of the anionic/cationic surfactant combination.[1]

III) This theory cannot uniquely account for the interactional features of surfactants in the mixed micelles.[281]

IV) If the regular solution theory is applicable to ionic/nonionic mixed micelles, the effective degree of counter-ion binding must be proportional to the mole fraction of ionic surfactant in the micelle, but this is contrary to the experimental observations.[282,283]

The micellar interaction parameter evaluated using Rubingh's theory[279] accounts well for the headgroup/headgroup interactions.

Maeda[284] suggested that besides the electrostatic interactions, the chain/chain interaction is also important and suggested a relationship by which chain/chain interaction can be computed. This chain/chain interaction becomes important in the mixed micelles when the hydrophobic group chain lengths are different. Maeda[284] extracted a contribution, B_1 which accounts for the standard free energy change when a non-ionic pure micelle is replaced by an ionic monomer; in addition to another interaction parameter, B_2 (an analog of the familiar interaction parameter 'β' in the regular solution approach) for mixed micelles. According to this approach, the thermodynamic stability (ΔG_m) is defined as a function of mole fraction of ionic component (X_2) by

$$\Delta G_m = RT(B_0 + B_1 X_2 + B_2 X_2^2) \tag{28}$$

$$where\ B_o = \ln C_1 \text{ (C_1 is the cmc of the nonionic surfactant)}, \tag{29}$$

$$B_1 + B_2 = \ln\left(\frac{C_2}{C_1}\right) \text{ (C_2 is the cmc of the ionic surfactant)}, \tag{30}$$

$$B_2 = -\beta^m \tag{31}$$

where all the quantities are on the unitary scale. One can evaluate B_1 from above expressions and hence ΔG_m.

We have showed that for a mixed cationic Gemini surfactant 1,4-butanediyl-α,ω-bis hexadecyl –dimethyl ammonium bromide (16-4-16) with $C_{12}E_6$, the free energy of micellization evaluated using phase seperation model tally with the Maeda.[201] Whereas higher negative values of B_1 were obtained, indicating that chain/chain interactions are important for the stability of the mixed micelle. Ruiz et al. [285] studied SDS/TX 100 mixed surfactant system and found an attractive interaction in this system. They also used Maeda's concept[284] and found that the chain/chain interaction in this system was very low. Gandhi et al.[114] carried out tensiometric studies on several binary surfactant mixtures containing anionic surfactants viz. metal (lithium, sodium, potassium, copper, cobalt and magnesium) dodecyl sulfates and a nonionic surfactant TX 100. Marked interaction is observed with monovalent dodecyl sulfates. The influence of counterion valence on the formation of mixed micelles indicated that mixed systems with bivalent counterions in metal dodecyl sulfate resembled nonionic/nonionic surfactant systems, where weak/negligible interaction is observed. Salt addition revealed the weakening of interaction in the mixed systems, which is due to the head group charge neutralization and the dehydration of ethylene oxide units of the nonionic surfactants.

Several other thermodynamic treatments for mixed micelle formation have been done by Scamehorn,[273] Geordiev,[285b] Blankschein,[285c] Nishikido[211], Kamrath and Franses.[285d] However in most of the cases the thermodynamic treatment assumed either a pseudophase separation (PPS) model or a mass action model.

I.17 NONIONIC SURFACTANTS AND DIMERIC (GEMINI) SURFACTANTS

I.17.1 Nonionic surfactants

During the last 3 decades, nonionic surfactants have increased their market share, to reach about 40% of the total surfactant production worldwide. Nonionic surfactants do not produce ions in aqueous solution. As a consequence, they are compatible with other type and are excellent candidates to enter complex mixtures, as found in many commercial products. They are much less sensitive to electrolytes, particularly divalent cations, than the ionic surfactants, and can be used in hard water. Their properties are very temperature dependent. Contrary to ionic surfactants they become less water soluble-more hydrophobic-at higher temperatures.

Nonionic surfactants are also good detergents, wetting agents and emulsifiers. Some of them have good foaming properties. Some categories exhibit a very low toxicity level and are used in pharmaceuticals, cosmetics and food products. Nonionic surfactants are found today in a large variety of domestic and industrial products, such as powdered or liquid formulations. However the market is dominated by polyethoxylated products. i.e. those whose hydrophilic group is a polyethyleneglycol chain produced by the polycondensation of ethylene oxide on a hydroxyl or amine group.

In the introduction section, it was maintained that a nonionic surfactant has a neutral hydrophilic part. This part can be of varying chemical composition, but here I will only describe those made from ethylene oxide, as the work presented in this thesis is based only on this type of surfactant.

Polyoxyethylene alkyl ethers, C_nE_m are nonionic surfactants comprising of an alkyl chain with methylene groups and a hydrophilic part with oxyethylene units. These compounds are of interest in their surface-active behaviour since they supply information complementary to that obtained with conventional ionic surfactants and because of their nonionic characters, are more amenable to theoretical treatment. These materials are commercially produced by reaction of ethylene oxide with an active hydrogen-containing compound using a catalyst. [286] In principle nonionic amphiphiles should have aggregation properties, which are easy to describe theoretically because the intra- and intermicellar head group interaction are much smaller than for ionic compounds. Since theoretical treatments with nonionic amphiphilies seem to be best suited for the check of theories. Nonionic polyoxyethylenated surfactants are also used extensively in the chemical industry in areas like health and personal care, coatings and polymers.

I.17.2 Gemini or dimeric surfactants

Gemini surfactants, some time referred to as twin surfactants or dimeric surfactants, have currently attracted a lot of attention in both academic and industrial research. [5-27] Gemini

surfactant contains two hydrophobic chains and two hydrophilic groups covalently attached through a spacer unit or in close proximity to the head groups. The spacer may be rigid or flexible, hydrophilic or hydrophobic, straight or branched, typically contains 2-8 bridging atoms.[25]

The name gemini was coined by Menger.[6] Since geminis were first synthesized and studied for their superior performance as catalysts in organic reactions,[287] a considerable number of investigations have been reported on their unusual physicochemical properties such as low cmc values (10 to 100 times lower than corresponding conventional surfactants),[288] greater efficiency in decreasing the surface tension of water (C_{20} values),[288,289] better wetting,[290]unusual micellar structure,[46] better solubilizing power,[291] low Kraft point,[19,288,291,292] better viscoelasticity, gelification and shear thickening[291] and enhanced properties for lowering the oil-water interfacial tension.[19] Cationic gemini dimeric surfactants are also capable of various biological activity[293,294] and have an effect on photosynthesis.[294] An arginine-based dimeric surfactant displayed a broad range of antimicrobial activity.[295] These dimeric surfactants are expected to be commercially used in the near future, probably as specialist surfactants[296] in the field of soil remediation, enhanced oil recovery, drug entrapment and release, etc.[290]

They are also useful as phase transfer catalysts[297] and in synthesizing ordered silicate mesoporous structure that are the analogs of lyotropic liquid crystals formed by the surfactants: hexagonal, cubic or lamellar.[298] Kirby et al[299] recently used the gemini surfactant in the gene transfection.

These surfactants are currently extensively investigated for their possible use in formulations mixing with ionic,[300,301] nonionic,[293-303] Zwitterionic[24,303] and sugar based surfactants.[111] The micellization behavior of alkanediyl-α,ω–bisalkyldimethylammonium bromide type dimeric surfactants has been the most investigated one.[15-17,19-22,91a,304,305]

The mixtures of these two different classes of surfactants will help in optimizing the physico-chemical properties as well as in formulating a detergent with low cmc values. Overall this will help in reducing the total amount of surfactant usage for a particular application and thus less impact on ecology and economy.

I.18 SCOPE OF THE PRESENT WORK

In complex world of surfactant formulation today, surfactant technologist needs to have the working knowledge of surfactant mixing principles as per the application desired for. To tailor the surfactant solution to best suit the desired application, one must be able to predict and manipulate, i) Micellization behaviour of surfactant unimer ii) shape and size distribution of the micelles, and iii) structure properties relation and iv) phase behaviour of surfactant solution.

The surface and morphological properties of surfactant in solution are very sensitive and are influenced or tuned to desired range, shape and application by altering the solvent polarity and type, temperature, pressure, *p*H, presence of various foreign substances (co-solvent) or proper choice of compatible surfactant mixture[1]. Control of the physicochemical, performance and morphological properties of such self aggregate by the addition of external component (additive/co-solute/co-surfactant) or by proper choice of surfactants mixture has become increasingly important in the recent years not only in the field of Chemistry but also in the fields of pharmaceutical and biotechnology for serious scientific and technological interest from both the theoretical and experimental point of view. Mixtures of surfactants form mixed micellar aggregates, which are superior to that of those of the individual components. Synergistic behaviour of mixed surfactants may be exploited to reduce the total amount of surfactant used in particular application resulting in reduction of cost and environmental impact.

Keeping in view of all these factors, we studied the properties of nonionic surfactant in presence of additives and binary surfactant mixture including cationic gemini surfactant at various mole fractions and at different temperatures. This will help us in understanding the underlying physics and chemistry of such systems and also in optimization and tuning the micellar solution properties for a desired application. Also to achieve a deep understanding of physico-chemical properties of micelle, both the dynamic and morphological properties must be achieved simultaneously. There is no single technique capable of yielding both types of information unambiguously. Hence in the work we combine both the studies in order to gather the related information.

Persegian[306] wrote the following sentences- "Despite enormous progress in understanding the genetics and biochemistry of molecular synthesis we still have only primitive ideas of how linearly synthesized molecules form the multi-molecular aggregates that are of cellular structures. We assume that the physical forces acting between aggregates of molecules and between individual molecules should explain many of their associative properties; but available physical methods have been inadequate for measuring or computing these forces in solids or liquids", in order to embrace and define a whole gray area of 'self assembly of amphiphilic molecules', that bridges chemistry, physics and biology, and which has been explored a lot in last five decades. Even though a lot of advancement has taken place in this field with development of newer instrumentation techniques and also due to efforts of researchers around the world, the knowledge and the understanding of the principles underlying micellization still seems to be low and thus his words seem to hold true even in present context after five decades. Still newer concepts are emerging and the area of micellization of amphiphilic molecules continues to grow at a brisk pace. The present thesis is one more attempt to shed light on principles underlying the fundamentals of micellization/self assembly of pure as well as mixed amphiphiles.

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