

CHAPTER-I

INTRODUCTION

A common characteristic property of the chemical substances is that they are either soluble in oil or in water. Substances, which are well soluble in water are usually poorly soluble in oil and are known as polar. Substances, which are well soluble in oil are often sparingly soluble in water and are called apolar. An **amphiphile** is a molecule composed of a polar and an apolar part. The polar part is generally referred to as the **head group** (hydrophilic), and the apolar part is known as the **tail** (hydrophobic). The word **amphiphile** is derived from the Greek words *amphi* (= both) and *philios* (= friend). So an amphiphilic molecule likes both oil and water. This combination of water- and oil-loving parts provides this class of substances with a range of interesting features. For example, they have the ability to form aggregates (known as micelles) and other self-assembled structures¹.

Surfactants

The amphiphiles that have the property of getting adsorbed onto the surfaces of a system thus modifying the interface free energies are referred to as surface-active-agents or surfactants. Such molecules have both hydrophilic and hydrophobic regions in their structures as illustrated schematically in Figure 1².

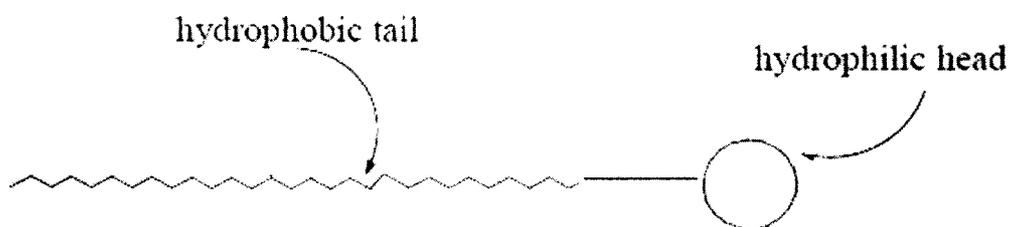


Figure 1. Structure of a surfactant

Most surfactants have a long hydrophobic tail that can be linear or branched which interacts only very weakly with the water molecules in an aqueous environment; hence the chain is called a hydrophobic tail. The hydrophilic head is a relatively small

ionic or polar group that interacts strongly with the water molecules via dipole-dipole or ion-dipole interactions.

Types of Surfactants

Surfactants can be classified according to their physical properties or functionalities. The following is the most common classification based on the nature of the head group.

Ionic surfactant: The head group of an ionic surfactant can be ionized in an aqueous solution. Depending on the outcome of this, there are a number of subcategories. If the charge on the head group is negative, the surfactant is said to be anionic. Among these, we find alkyl sulfates³, alkyl sulphonates⁴, alkyl phosphates^{5, 6} and fatty acid salts^{7, 8} (see Figure 2, for example). If the residual charge is positive, the surfactant is cationic and common examples of this kind are alkyltrimethylammonium^{10, 11} and alkylpyridinium halides¹², an example of which is shown in Figure 2.

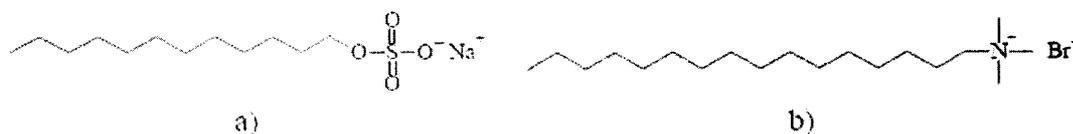


Figure 2. Molecular structure of two common ionic surfactants

a) Sodium dodecylsulfate (SDS)

b) Hexadecyltrimethylammonium bromide (CTAB)

In some surfactant molecules the ionization leads to two separate groups of opposite charges attached to the hydrophobic part^{13, 14}. Such surfactants are called zwitterionic and these are common in biological systems¹⁴. This type of surfactant can also be regarded as nonionic, since their total charge is zero. Catanionic surfactants (Figure 3) consist of oppositely charged surfactant ions, *i.e.*, one surfactant acts as counterion to the other¹⁵⁻¹⁷. Catanionic surfactants can be either symmetric (both alkyl chains are of the equal length) or asymmetric (one chain is shorter than the other).

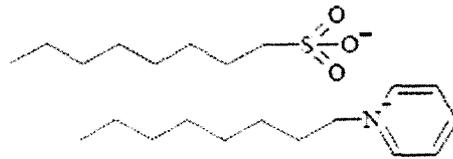


Figure 3. A symmetric catanionic surfactant, octylpyridinium octanesulphonate (OPOS)

Nonionic surfactant: As the name implies, nonionic surfactants lack groups that can easily be ionized. Examples of nonionic surfactants with a polyoxyethylene^{18, 19} and a polyhydroxy^{20, 21} moiety are shown in Figure 4. Compared to ionic surfactants of comparable size, nonionic surfactants form aggregates at lower concentration and the aggregation behaviour is less sensitive to the added salt due to the absence of repelling charges in the head groups.

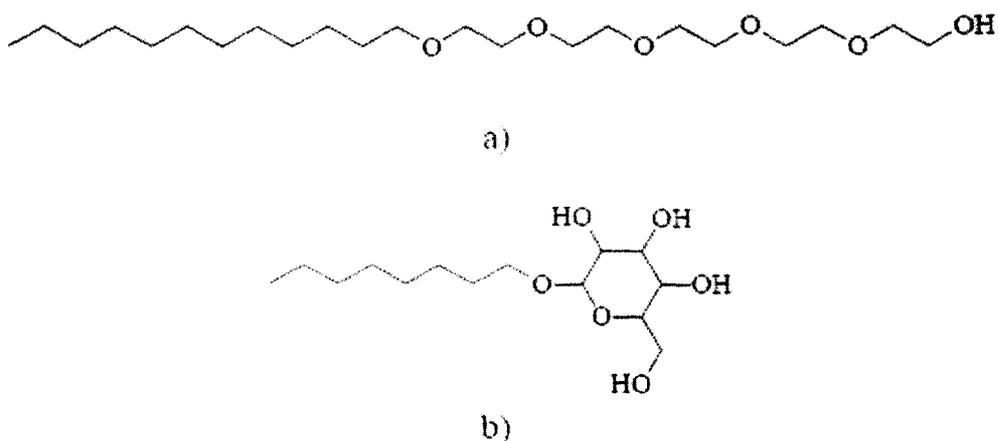


Figure 4. Nonionic surfactants:

- a) Pentaoxyethylene dodecyl ether ($C_{12}E_5$)
- b) n-octyl β -D-glucoside (OG)

Different Types of Aggregates

Micelles: In aqueous solution a micelle is a cluster of surfactants, usually pictured as a spherical particle with a water-free core containing all the tails, and an outer shell

containing the head groups, some water molecules and some of the counterions (Figure 5).

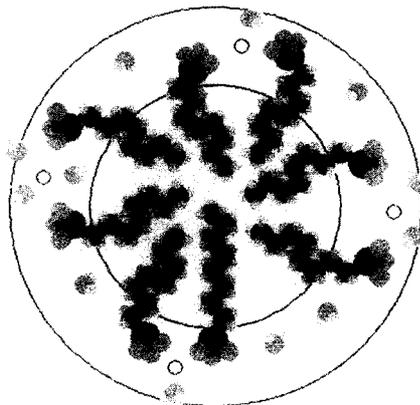


Figure 5. A schematic representation of a micelle showing the hydrocarbon core (inner circle) and head group layer (outer circle) with associated counterions and water molecules.

Micelle formation occurs only beyond a critical concentration of the amphiphiles, referred to as the critical micelle concentration or *cmc*. The formation of micelles, like all self-assembly processes, is governed by thermodynamics, *i.e.*, micelle formation occurs because the system minimizes its Gibbs free energy in the process. Below the *cmc*, surfactants are present as monomers or dimers. Short-chain surfactants can behave like hydrotropes and form less well-defined micellar aggregates. A number of different more complex micellar structures also exist. They can grow lengthwise, forming rod-like²², thread-like or worm-like micelles²³. These micelles, can in turn entangle forming networks^{23, 24}.

Vesicles: Another type of aggregate that can be found in dilute solutions is the vesicle.

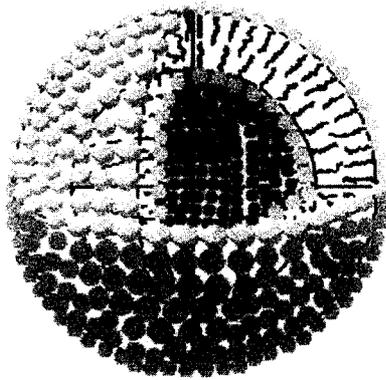


Figure 6. A schematic representation of a vesicle.

A vesicle is a shell^{25, 26}, consisting of a surfactant bilayer, which encapsulates an aqueous interior (Figure 6). These structures can be very large (>100 nm). Vesicles can form inside each other, similar to a Russian doll. Such a particle is called an onion or a multi-lamellar vesicle. Due to the bilayer structure, a vesicle is more related to the lamellar phase than to a micelle. In fact vesicles can be formed by agitating a lamellar phase²⁷. Reverse vesicles have also been found in a phospholipids/triolein/water system²⁸.

Micellar Shape

The structure of a micelle is dictated by the equilibrium between the repulsive forces among hydrophilic head groups and attractive forces among hydrophobic tails. Several structures have been proposed for the micelles. McBain proposed a coexistence of the spherical and lamellar micelles²⁹. Hartley suggested that micelles are spherical entities with charged groups located at the micellar surface³⁰. The Hartley model successfully describes many properties of micellar systems. According to this model, counterions are bound to the charged head groups of the surfactants. Hartley proposed that the inner cores of the micelles have properties of liquid hydrocarbons; thus, micelles are able to solubilize hydrophobic molecules that are otherwise insoluble^{31, 32}. Debye and Anacker proposed rod-shaped micelles rather than spherical or disk-like ones³³. Based on NMR and kinetic studies, Menger reports that micelles are more disorganized with chain looping, nonradial distribution of

chains, and contact of terminal methyl groups with water³⁴. According to the Menger model, micelles have rough surface with water-filled pockets. In general, the spherical form is accepted as the true representation of the micelle (Figure 7).

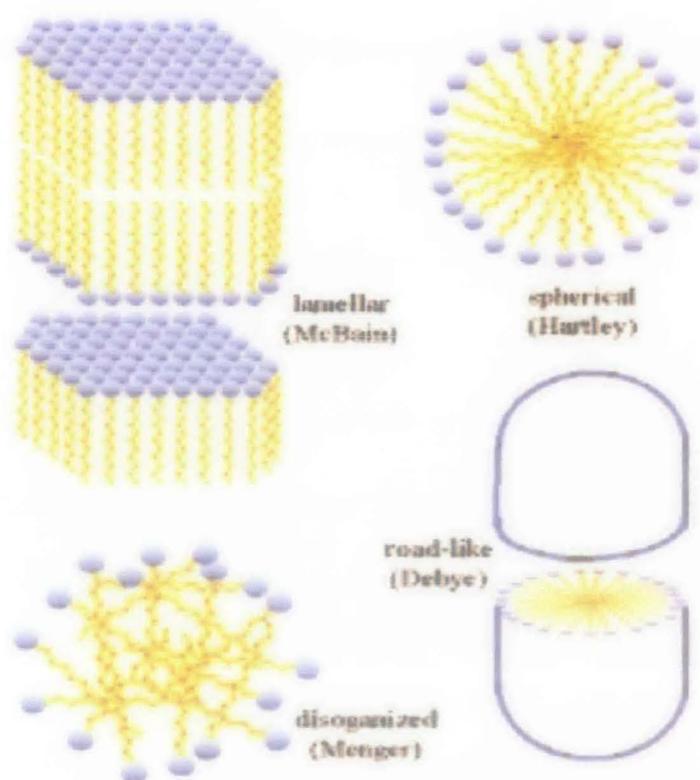


Figure 7. Different proposed structures of a micelle.

With increasing surfactant concentration, the shape of ionic micelles changes in the sequence: spherical - cylindrical - hexagonal - lamellar³¹ (Figure 8). Additional factors that affect the micelle shape are the optimal head group area, the volume, and the chain length of the tail³⁵.

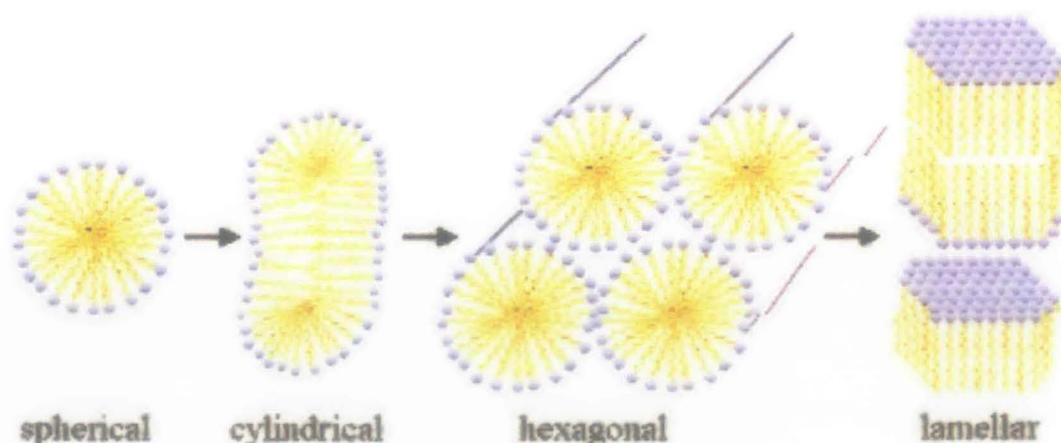


Figure 8. Change in micelle shape with respect to the change in surfactant concentration.

The generalized structure of the cross-section of a typical micelle is assumed to have a liquid core formed by the associated hydrocarbon chains with ionic or polar head groups projected out into the water. In ionic micelles, the Stern layer consists of bound ionic surfactant head groups, counterions, and water molecules. The thickness of the Stern layer is usually only a few angstroms. Figure 9 shows different regions of a spherical micelle. The layer just beyond the Stern layer is a diffuse layer (known as the Guoy-Chapman layer) extending outward to several hundred angstroms. The inner core of the micelle is usually divided into two regions. The hydrophobic tail of the surfactant forms a water free region (inner core). Moving outward from the inner core of the micelle, there is a hydrated region between the inner core and the polar head group of the micelle. This hydrated region is called the palisade layer and is viewed as liquid hydrocarbon. The radius of the inner core and the palisade layer is approximately equal to the length of the fully extended hydrocarbon chain³⁶.

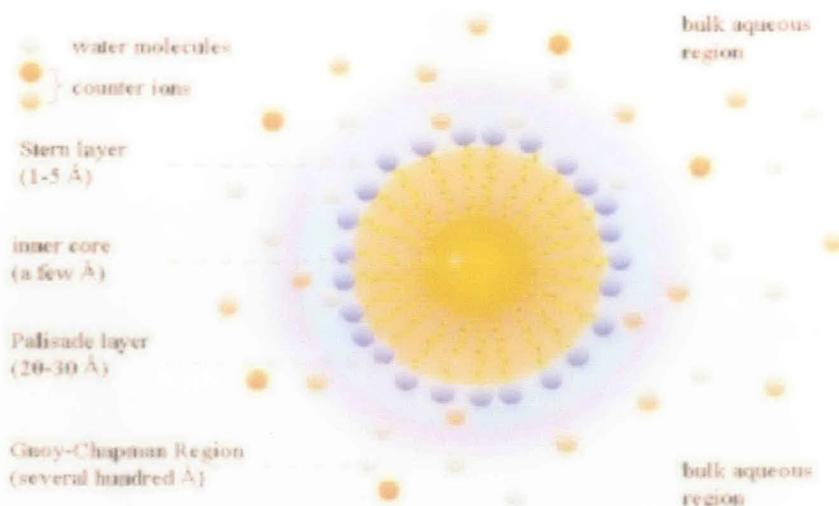


Figure 9. Important micellar regions.

Critical Micelle Concentration (*cmc*) and its Determination

In dilute solutions, surfactant molecules exist as individual species in the media and the solutions have completely ideal chemical and physical properties. As the surfactant concentration increases, chemical and physical properties of the solutions deviate from ideality by varying degrees, and at a certain concentration, aggregation of the surfactant monomers occurs and micelles are formed. This concentration is called the critical micelle concentration (*cmc*)². The critical micelle concentration indicates usually a narrow range of concentrations separating the limits below which most of the surfactant is in the monomeric state and above which virtually all additional surfactant molecules enter the micellar state³⁷.

The *cmc* is a very important solution property of surfactants. Its determination thus requires a special mention. There exist a large number of experimental methods for determining the value of *cmc*. Mukerjee and Misels³⁸ reviewed about 70 methods which have been published for *cmc* determination. The appropriate choice of the method depends upon the availability of the various techniques, the relationship between the technique and the ultimate application, and the personal preferences of the investigator. Many techniques have been used for this purpose including surface tension, osmotic pressure, turbidity, conductivity, capillary electrophoresis, light scattering, spectroscopic techniques including fluorescence^{35, 39-48}. The most

frequently used methods are surface tension, conductivity and fluorescence. The conductivity method is applicable only to ionic surfactants. The critical micelle concentrations of surfactant solutions measured by different methods demonstrate a distinct feature on the change in concentration dependence of the physicochemical properties around the critical micelle concentration as shown in Figure 10.

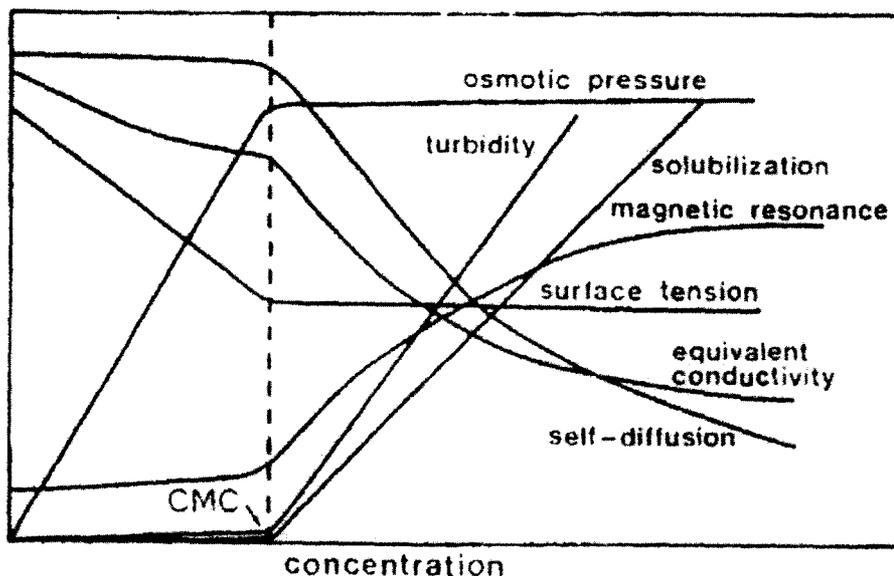


Figure 10. Change in concentration dependence of a wide range of physico-chemical quantities around the critical micelle concentration (After Lindman *et al.*⁴⁹).

The properties show breaks in the plots which are considered as the *cmc* points for the surfactant under investigation. It is to be noted that the *cmc* values determined by different methods fall within a narrow range, *i.e.*, the *cmc* is moderately method dependent. It may be mentioned in this context that the acceptance limit of variation of *cmc* is within $\pm 10\%$.

Factors Affecting Micelle Formation and *cmc*

The hydrophobic chain length: The *cmc* decreases strongly as the length of the hydrophobic part of the surfactant is increased, the decrease being more rapid for nonionic than for ionic surfactants⁵⁰. For a straight chain hydrocarbon surfactant of about 16 carbon atoms or less bound to a single terminal head group, the *cmc* is

usually reduced to approximately half of its previous value with the addition of each methylene group⁴². An even more pronounced decrease in *cmc* with the increase of hydrocarbon chain length has been noted with nonionic surfactants; the addition of one methylene group causes the *cmc* to decrease to one third of its original value⁵¹. The *cmc*s of various homologues of surfactants with a linear alkyl chain follow the equation⁵²,

$$\log cmc = A - Bn \quad (1)$$

where *n* is the number of carbon atoms in the alkyl chain and *A* and *B* are constants specific to the homologous series under a given conditions of constant temperature, pressure etc. Figure 11 shows a linear relationship between $\log cmc$ and the number of carbon atoms in the alkyl chains. For chains containing more than 16 carbon atoms, this relationship no longer holds and further increase in chain length often has no appreciable effect on the *cmc*, possibly due to the coiling of the long chains in solutions⁵³. In case of branched hydrocarbon chains, the effect on the *cmc* is not higher than that for straight chain surfactants. For a given alkyl chain, *cmc* increases in the order: nonionic < zwitterionic < ionic (cationic or anionic)³⁸.

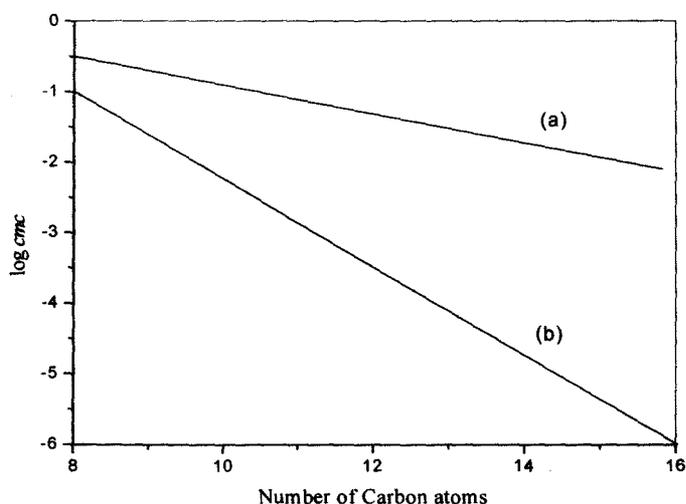


Figure 11. Variation of *cmc* with the hydrocarbon chain length for (a) sodium alkyl sulfate and alkyltrimethylammonium bromide (b) hexaoxyethylene monoalkyl ethers (After Attwood and Florence⁴²).

Temperature: The effect of temperature changes on the *cmc* of surfactants in aqueous solution have been found to be quite complex. For ionic surfactants, the *cmcs* show a parabolic-type variation with temperature passing through a minimum⁵⁴. The minimum in the curve for ionic surfactants occurs typically between 20 and 30 °C. At lower temperatures (generally at 30 °C or below) the *cmc* decreases with increasing temperature, which is probably due to desolvation of parts of monomer which make it hydrophobic, whilst further rise in temperature causes disruption of the water structure around the hydrophobic groups which opposes micellization⁴². A decrease in the micelle size of ionic surfactants with the increase in temperature has also been reported⁵⁵.

Temperature dependence of the *cmcs* for nonionic surfactants is not so predictable, although it has been found that some nonionic surfactants show a *cmc* minimum⁵⁶ around 50 °C. The most drastic effect of temperature on nonionic surfactants is that on solubility. Nonionic surfactants form isotropic solutions below a lower Krafft point and upper cloud point. Heating a clear solution to above the cloud point causes a reversible phase separation: a phase rich in surfactant separates out of solution leaving an aqueous phase containing surfactant monomers.

Effect of additives: A survey of literature shows that additives have a marked effect on the *cmcs* of both ionic and nonionic surfactants⁵⁷⁻⁶⁰. Paradas *et al.*⁵⁹ have shown that there is a large decrease in the *cmcs* of CTAB and SDS in presence of 0.1M NaCl but no significant change was observed in the *cmc* value of polyoxyethylene-*tert*-octylphenylether (Triton X-100 or TX-100). In general, the addition of electrolytes strongly reduces the *cmc* for ionic surfactants, but this has little effect on the *cmcs* of nonionics⁴⁹. Addition of an electrolyte causes a reduction in the thickness of ionic atmosphere surrounding the polar head groups which consequently decreases repulsion between them. These effects are manifested in the reduction in *cmc* and in the increase in the aggregation number. For ionic surfactants, the effect of addition of electrolyte with the same charge as the native counterion on the *cmc* can be empirically quantified with the relationship⁶¹

$$\log_{10} cmc = -a \log_{10} C_c + b \quad (2)$$

where *a* and *b* are constants for a given ionic head group at a particular temperature, and *C_c* is the total concentration of monovalent counterion in molarity.

The critical micelle concentration of nonionic surfactants in aqueous solutions is lowered by the addition of most inorganic salts^{57, 62-64}. The observed changes in the *cmc* of nonionic and zwitterionic materials on the addition of electrolytes cannot be attributed to the same electrostatic effect as that for fully ionic surfactants.

Large amount of small polar organic molecules *e.g.*, ethanol, urea, etc. raises the *cmc*^{65, 66}. The studies on the effect of *n*-alcohols on the aggregation number *n* of ionic surfactants suggest that water-soluble alcohols (methanol to butanol) are predominantly dissolved in the water phase and that the aggregation numbers may increase or decrease depending upon the alcohol concentration⁶⁷. The effect of added alcohols has been reported for nonionic systems, where methanol and ethanol cause an increase in *cmc* and higher alcohols butanol and pentanol cause a decrease in *cmc*^{68, 69}.

Pressure: Studies have been made on the pressure effect on the *cmc* by different techniques⁷⁰⁻⁷⁴. Increases in pressures initially retards the association and after a threshold value (100-200 Mpa), the process is favoured. This is a consequence of water structure disruption by the applied thrust to assist wider distribution of the surfactant molecules in solution to oppose their tendency of association. The release of surfactant monomers from the micelles in the lower range of pressure and their association at higher pressure together with the changed dielectric constant of the solution by the application of pressure also play their specific roles in surfactant organization. This has been supported by the measurement of aggregation number⁷⁵, which shows a minimum for ionic surfactants with respect to pressure.

Counterion effect: A number of studies⁷⁶⁻⁸⁰ indicate that counterions associated with an ionic surfactant have pronounced effect on the micellar properties. Since electrostatic repulsion among the ionic groups would be the greatest for complete ionization, it is not surprising to find that the *cmc* of surfactant in aqueous solution decreases as the degree of counterion binding increases. From regular solution theory (please see later), it is found that the extent of ion pairing in a system will increase as the polarizability and the valence of the counterions increase. Conversely, a larger radius of hydration will result in greater ion separation. It has been found that, for a given hydrophobic tail and anionic head group, the *cmc* decreases in the order, $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{N}(\text{CH}_3)_4^+ > \text{N}(\text{CH}_2\text{CH}_3)_4^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+}$. In the case of cationic

surfactants such as dodecyltrimethylammonium halides, the *cmc*s are found to decrease in the order $F^- > Cl^- > Br^- > I^-$ ⁵².

Effect of polar head group: As mentioned earlier, the more the ionization of the surfactants, the higher the *cmc*, due to the increase in electrical work required to form the micelle⁸¹. However, nonionic surfactants have much lower *cmc* than ionic surfactants⁸². The lower *cmc*s of the nonionic surfactants are a consequence of the lack of electrical work necessary in the formation of micelles⁴².

A detailed study on the effect of the nature of the polar group of ionic surfactants on the micellar properties has been reported by Anacker and co-workers⁸³⁻⁸⁵. They concluded that the mean distance of closest approach of a counterion to the charged centre of the surfactant was an important factor determining the micellar size. For example, decylammonium bromide forms much larger micelles than decyltrimethylammonium bromide because Br^- counterions are able to approach more closely to the charged nitrogen atom of decylammonium bromide thus effectively shielding the repulsive electrical forces⁸³. The effect of changing the charge-bearing atom in the polar head group has also been reported⁸⁴. Replacement of nitrogen in decyltrimethylammonium bromide by phosphorus or arsenic causes an increase in the aggregation number with a corresponding decrease in *cmc*.

In polyoxyethylated ether type of nonionic surfactants, increase of polyoxyethylene chain length causes an increase in the *cmc* and decrease in the micellar size⁴². Increase in the polyoxyethylene chain length makes the monomer more hydrophobic giving higher *cmc*.

Thermodynamics of Micelle Formation

Micellization is a spontaneous process and like all other spontaneous physicochemical processes micellization is energetically controlled and guided by the thermodynamic principles. During the process of micellization, 'iceberg' structure of water molecules surrounding the nonpolar hydrocarbon tail of the surfactant is broken with a resultant gain in entropy⁸⁶⁻⁸⁸.

During the past years, significant advances have been made on the ways to calculate the changes in the thermodynamic parameters that accompany micelle formation from experimental data⁸⁹⁻⁹³.

Many workers⁹⁴⁻⁹⁸ paid considerable attention to the thermodynamics of micellization, and in particular to the merits and demerits of various approaches which have been made to this problem.

Two basic approaches that have been made to explain the thermodynamics of micelle formation have gained predominance and these have been generally accepted as useful models^{95, 99-105}. These are (i) the mass action model, and (ii) the phase separation or pseudophase model.

The Mass Action Model: According to the mass action model, micelles and unassociated surfactant ions are assumed to be in association-dissociation equilibrium. The mass action approach was originally applied mainly to ionic surfactants^{103, 104, 106}. Application of this model to nonionic surfactants has been discussed by Corkill *et al.*¹⁰⁷.

(a) Application of mass action model to nonionic surfactants: According to the mass action model, micelles, M , are considered to be formed by a single step reaction from n monomers, S , as,



where, K_M is the equilibrium constant for micelle formation given by

$$K_M = \frac{a_M}{a_S^n} \quad (4)$$

where a terms represent the activities of the relevant species.

Assuming ideality, we may write, as an approximation,

$$K_M = \frac{x_M}{(x_S)^n} \quad (5)$$

where x_M and x_S are the mole fractions of micelle and monomers respectively.

The standard Gibbs free energy of micellization is given by the relation,

$$\Delta G_M^0 = -RT \ln K_M = -RT \ln x_M + nRT \ln x_S \quad (6)$$

The change of free energy per mole of the monomeric unit is then,

$$\Delta G_m^0 = \frac{\Delta G_M^0}{n} = -\frac{RT}{n} \ln x_M + RT \ln x_S \quad (7)$$

At *cmc*, the percentage of monomers undergoing micellization is very small. Therefore, at *cmc* by conceptual approximation,

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (8)$$

(b) Application of mass action model to ionic surfactants: The ionic micelle, $M^{\pm(n-m)}$, is considered to be formed by the association of n surfactant ions, S^\pm , and m firmly bound counterions, X^\pm .



Hence,
$$K_M = \frac{a_{M^{\pm(n-m)}}}{a_{S^\pm}^n a_{X^\pm}^m} \approx \frac{x_{M^{\pm(n-m)}}}{x_{S^\pm}^n x_{X^\pm}^m} \quad (10)$$

The standard Gibbs free energy of micellization is given by,

$$\Delta G_M^0 = -RT \ln K_M = -RT \ln x_{M^{\pm(n-m)}} + nRT \ln x_{S^\pm} + mRT \ln x_{X^\pm} \quad (11)$$

Therefore, the free energy per mole of monomeric unit,

$$\Delta G_m^0 = \frac{\Delta G_M^0}{n} = -\frac{1}{n} RT \ln x_{M^{\pm(n-m)}} + RT \ln x_{S^\pm} + \frac{m}{n} RT \ln x_{X^\pm} \quad (12)$$

Again, since the percentage of monomers undergoing micellization is very small and n is usually large, so

$$\Delta G_M^0 = RT \ln x_{S^\pm} + \frac{m}{n} RT \ln x_{X^\pm} \quad (13)$$

If normal electrolyte is used then,

$$x_{S^\pm} = x_{X^\pm} \quad (14)$$

So, at cmc ,
$$x_{S^\pm} = x_{X^\pm} = x_{cmc} \quad (15)$$

Thus,
$$\Delta G_m^0 = \left(1 + \frac{m}{n}\right) RT \ln x_{cmc} = (1 + \beta) RT \ln x_{cmc} \quad (16)$$

where β = fraction of counterions bound.

If $m = 0$ i.e., no counterions bound, as in the case of nonionic surfactants,

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (17)$$

For 100% counterion binding, $\beta=1$ and

$$\Delta G_m^0 = 2RT \ln x_{cmc} \quad (18)$$

The above relations are based on constancy of n and several other valid approximations.

The Pseudophase Model: In the pseudophase model the micelles are considered to form a separate phase at and above the cmc . Thus monomer concentration remains

unchanged at and above cmc , *i.e.*, with increasing surfactant concentration, only micelles are formed.

(a) Application of pseudophase model to nonionic surfactants: To calculate the thermodynamic parameters for the micellization process, we are required to define the standard state. For a surfactant in the micellar state, the micellar state itself is considered to be the standard state.

At constant temperature, if μ_s and μ_m are the chemical potentials of the unassociated surfactant in the aqueous phase and associated surfactant in the micellar phase respectively, and since these two phases are in equilibrium:

$$\mu_s = \mu_m \quad (19)$$

For a nonionic surfactant,

$$\mu_s = \mu_s^0 + RT \ln a_s \quad (20)$$

Assuming the concentration to be low, the activity of surfactant monomer, a_s , may be replaced by the mole fraction of monomer S , x_s ,

$$\mu_s = \mu_s^0 + RT \ln x_s \quad (21)$$

where μ_s^0 is the chemical potential of the surfactant monomer in the standard state.

Since the micellar material is in its standard state, one can write

$$\mu_m = \mu_m^0 \quad (22)$$

The standard Gibbs free energy change for the transfer of one mole of surfactant from solution to micellar phase,

$$\begin{aligned} \mu_m = \mu_m^0 - \mu_s^0 &= \mu_m - \mu_s + RT \ln x_s \\ &= RT \ln x_s \end{aligned} \quad (23)$$

Assuming that the concentration of free surfactant in the presence of micelle is constant and is equal to the cmc value, x_{cmc} , then the free energy per mole of monomer is given by

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (24)$$

(b) Application of pseudophase model to ionic surfactants: In case of an ionic surfactant to calculate ΔG_m^0 , it is necessary to consider not only the transfer of surfactant monomers from the aqueous to micellar phase but also the transfer of m/n

moles of counterions from the standard state to the micelle. Equation (23) is thus written as,

$$\Delta G_m^0 = RT \ln x_s + \frac{m}{n} RT \ln x_x \quad (25)$$

where x_s and x_x are the mole fractions of surfactant ion and counterion respectively. Assuming the concentration of free surfactant and counterion in the presence of micelle to be constant and equal to the *cmc* value, x_{cmc} , then

$$\Delta G_m^0 = \left(1 + \frac{m}{n}\right) RT \ln x_{cmc} = (1 + \beta) RT \ln x_{cmc} \quad (26)$$

where β is the fraction of counterions bound to the micelle.

Thus we get the same equation for ΔG_m^0 for nonionic and ionic micelles as we get in the case of mass action model. The two equations differ slightly because of the differences in the way in which the mole fractions are calculated. In the mass action model, the total number of moles present at the *cmc* is equal to the sum of the moles of water, surfactant ions, micelles, and free counterions whereas total number of moles in the pseudophase model is equal to the sum of moles of water and surfactant. Applying Gibbs-Helmholtz equation and assuming the aggregation number, n , to be large and independent of temperature, the standard enthalpy of micellization (ΔH_m^0) at constant pressure, P , is given by

$$\Delta H_m^0 = -(1 + \beta) RT^2 \left[\frac{\partial \ln x_{cmc}}{\partial T} \right]_P = (1 + \beta) R \left[\frac{\partial \ln x_{cmc}}{\partial (1/T)} \right]_P \quad (27)$$

for ionic micelles, and

$$\Delta H_m^0 = -RT^2 \left[\frac{\partial \ln x_{cmc}}{\partial T} \right]_P = R \left[\frac{\partial \ln x_{cmc}}{\partial (1/T)} \right]_P \quad (28)$$

for nonionic micelles.

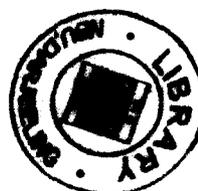
Finally, the standard entropy of micellization per mole of monomer, ΔS_m^0 , may be obtained from

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (29)$$

For the evaluation of ΔH_m^0 and ΔS_m^0 , the *cmc* should be measured at different temperatures and treated according to the Equations (27) to (29). The ΔS_m^0 values are normally positive; negative values are seldom obtained^{108, 109}. Micellization process, therefore, ends up with an increase in entropy; an overall disordered state is

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envisaged. This is due to the release of solvent molecules attached with the nonpolar tails of surfactant monomers by hydrophobic hydration during self organization, the entropy gain by the process exceeds the loss by amphiphilic association, solvation etc., making the overall entropy change positive.

Neither the mass action model nor the pseudophase model for micellization is exactly correct. In both the approaches, at *cmc*, the equilibrium concentration of free monomer is considered equivalent to *cmc*. It is also considered that the aggregation number and counterion binding of micelles are not affected by temperature variation at least within the range of measurements. But despite these limitations, both the mass action and pseudophase models are useful representations of the micellar process and may be used to derive equations relating the *cmc* to the various factors that determine it. There are some other approaches also for the determination of energetics of micellization. Thermodynamics of small-systems have been developed by Hill¹¹⁰. Hall and Pethica⁹⁵ have applied it to non-ionized and non-interacting systems. In this approach the aggregation number is treated as a thermodynamic variable, thereby enabling variations in the thermodynamic functions of micelle formation with the mean aggregation number. A more detailed treatment of multicomponent micelle, describing systems of interacting aggregates, has been developed by Hall^{96, 111-113}.

Another approach to small-system thermodynamics has been formulated by Corkill and co-workers¹¹⁴⁻¹¹⁶ and applied to systems of nonionic surfactants. This multiple-equilibrium model considers equilibria between all micellar species present in solution rather than a single micellar species as was considered by mass action theory.

An interesting model of micelle formation based on geometrical considerations of micelle shape has been proposed by Tanford¹¹⁷ and later extended by Israelachvili *et al*⁹³.

This approach has been further developed by Ruckenstein and Nagarajan⁸⁹. Such an approach is useful for application where the chemical structure of the surfactant is of central importance. The constraints of changing micellar shape and size, variation of counterion association and micellar solvation with temperature and other environmental changes provide challenge to the exactness of the energetic parameters and make the topic worthy of further investigation.

Mixed Micelles

Surface-active compounds used in commercial applications typically consist of a mixture of surfactants because they can be produced at a relatively lower cost than isomerically pure surfactants. In addition, in many surfactant applications, mixtures of dissimilar surfactants often exhibit properties superior to those of the constituent single surfactants due to synergistic interactions between the surfactant molecules¹¹⁸. For example, the critical micelle concentration (*cmc*) of a mixture of anionic and cationic surfactants in aqueous solutions is considerably lower than the *cmc* of each of individual surfactant¹¹⁹. On the other hand, antagonistic interactions in a mixture of hydrocarbon-based and fluorocarbon-based surfactants in aqueous solution result in a mixed system whose *cmcs* are considerably higher than the *cmcs* of the constituent single surfactants^{120, 121}. In general, specific interactions (synergistic or antagonistic) between surfactants result in solutions of surfactant mixtures having micellar and phase behavior properties which can be significantly different from those of the constituent single surfactants. Thus physicochemical studies are required for mixed micelles of ionic-ionic, ionic-nonionic and nonionic-nonionic combinations for formulations, uses and basic understanding.

Theory of Binary Mixed Micelle Formation

By adopting the phase separation model for micellization, a simple theory which treats mixed micelle as an ideal mixture of its components and considers the activity coefficient of free surfactant monomers equal to unity, was proposed by Clint^{122, 123} to predict the *cmc* of the mixture in the form of the following equation,

$$(1/cmc_C) = \sum_{i=1}^n (\alpha_i / cmc_i) \quad (30)$$

Here, α_i denotes the stoichiometric mole fraction of the *i*th component in solution, respectively. The terms cmc_i and cmc_C are the critical micellar concentrations of the *i*th component and the mixture, respectively. According to this model the *cmc* represents the concentration at which the pseudo-phase (mixed micelle) first forms through a process analogous to phase separation. In the ideal-mixing model, the mixture *cmc* was found to be only a function of the *cmcs* of the constituent single surfactants and the composition of the mixture. Ideal-mixing models have been quite successful in predicting the *cmc* of aqueous solutions of binary nonionic¹²⁴⁻¹²⁶ and

binary ionic^{122, 127, 128} surfactants that belong to a homologous series. On the other hand, in solutions which contain two or more non-homologous surfactant species, the measured *cmc*s were often found to be substantially lower than those predicted by the ideal-mixing models^{119, 129, 130}. The observed deviations from ideality were attributed to nonideal mixing effect arising from specific interactions between the different surfactants present in mixed micelle. Later on, various theories for mixed micellization have been put forward¹³¹⁻¹³⁷. We are giving here a brief account of these theories.

Rubingh's theory: According to Rubingh's¹³³ treatment, if two surfactants 1 and 2 form a mixed micelle, the mole fraction X_R of the surfactant 1 in the micelle can be estimated from a knowledge of the critical micelle concentration (*cmc*) of the component surfactants cmc_1 and cmc_2 , the *cmc* of the mixed surfactant, cmc_{mix} , and the mole fraction of the surfactant 1 in the total mixed solute, through the equation

$$\frac{(X_R)^2 \ln[cmc_{mix} \alpha_1 / cmc_1 X_R]}{(1 - X_R)^2 \ln[cmc_{mix} (1 - \alpha_1) / cmc_2 (1 - X_R)]} = 1 \quad (31)$$

From the X_R value its convenient to calculate the interaction parameter, β , and the quantities f_1 and f_2 :

$$\beta = (1 - X_R)^{-2} [\ln(cmc_{mix} \alpha / cmc_1 X_R)] \quad (32)$$

$$f_1 = \exp[\beta(1 - X_R)^2] \quad (33)$$

$$f_2 = \exp[\beta(X_R)^2] \quad (34)$$

where f_1 and f_2 are the activity coefficient of surfactants 1 and 2 respectively in the mixed micelle. The interaction parameter β is a measure of interaction between the components in the micelle (assumed to be constant) which can be obtained from the experimental data.

Motomura's theory: Motomura and co-workers¹³² have shown that the process of mixed micellization can be treated from the view point of thermodynamics. According to this approach, micellization is considered similar to a macroscopic bulk phase, and energetic parameters associated with the process are expressed by excess thermodynamic quantities. The behavior of surfactant molecules in the micelle bears resemblance to that in the adsorbed film.

For a binary mixture of surfactants, Motomura *et al.* considered that surfactant 1 dissociates giving ν_{1a} anions and ν_{1c} cations, while surfactant 2 dissociates giving ν_{2b} cations and ν_{2d} anions and the following relations hold

$$\hat{X}_2 = \nu_2 X_2 / (\nu_1 X_1 + \nu_2 X_2) \quad (35)$$

$$\hat{cmc} = (\nu_1 X_1 + \nu_2 X_2) cmc \quad (36)$$

$$X_M = \frac{\hat{X}_2 - (\hat{X}_1 \hat{X}_2 / \hat{cmc})(\partial \hat{cmc} / \partial \hat{X}_2)_{P,T}}{1 - \delta_d^c \nu_{1c} \nu_{2d} / (\nu_{1c} \nu_2 \hat{X}_1 + \nu_{2d} \nu_1 \hat{X}_2)} \quad (37)$$

where subscripts 1 and 2 refer to surfactants 1 and 2 respectively, X stands for the mole fraction, ν represents the number of ions contributed by a surfactant, the parameters with subscript M represent their state in the micelle, and δ_d^c is the Kroeneker delta defined by $\delta_d^c = 0$ when $d \neq c$ and $\delta_d^c = 1$ when $d = c$. In case of cationic-anionic, anionic-anionic combinations ($\nu_{1a} = \nu_{1c} = \nu_{2b} = \nu_{2d} = 1$), $\hat{X}_2 = X_2$, $\hat{cmc} = 2cmc$ and

$$X_M = \hat{X}_2 - 2(\hat{X}_1 \hat{X}_2 / \hat{cmc})(\partial \hat{cmc} / \partial \hat{X}_2)_{P,T} \quad (38)$$

For nonionic-nonionic pairs ($\nu_{1a} = \nu_{2b} = 1, \nu_{1c} = \nu_{2d} = 0$), $\hat{X}_2 = X_2$, $\hat{cmc} = cmc$ and for cationic-nonionic pair ($\nu_{1a} = \nu_{1c} = 1; \nu_{2b} = 1; \nu_{2d} = 0$), $\hat{X}_2 = 2X_1 / (X_1 + 2X_2)$, $\hat{cmc} = (X_1 + 2X_2)cmc$ and

$$X_M = \hat{X}_2 - (\hat{X}_1 \hat{X}_2 / \hat{cmc})(\partial \hat{cmc} / \partial \hat{X}_2)_{P,T} \quad (39)$$

The determination of $\partial \hat{cmc} / \partial \hat{X}_2$, i.e., the slope of the \hat{cmc} vs. \hat{X}_2 plot then leads to the evaluation of X_M (mole fraction of a component) in the mixed micelle.

Sarmoria and Puvvada's theory: Sarmoria *et al.*¹³⁶ and Puvvada *et al.*¹³⁷⁻¹³⁹ have proposed a molecular thermodynamic model which is applicable to mixed binary solutions of non-ideal surfactant combinations based on the *cmc*s of the component surfactants, the concentrations of the surfactants, the chemical structure of the

hydrophobic and hydrophilic moieties of the individual surfactants, and other solution conditions *e.g.*, temperature, the type and concentration of salts present. Several equations have been derived to calculate the relevant physicochemical quantities¹³⁶. Equation (30) has been modified and the following equations have been proposed

$$(1/cmc_{\text{mix}}) = (\alpha_1 / f_1 cmc_1) + ((1 - \alpha_1) / f_2 cmc_2) \quad (40)$$

$$f_1 = \exp \left[\left\{ \beta_{12} (1 - \alpha^*)^2 \right\} / kT \right] \quad (41)$$

$$f_2 = \exp \left[\left\{ \beta_{12} (\alpha^*)^2 \right\} / kT \right] \quad (42)$$

where f_1 and f_2 are the activity coefficients of component 1 and component 2 in the mixed micelle, β_{12} is the predicted interaction parameter between the surfactant 1 and 2, α^* is the optimal micellar composition where the free energy of micellization attains its minimum value, k is the Boltzmann constant, and T is the temperature in absolute scale. The predictive quantity β_{12} based on fundamental considerations was obtained from the relation,

$$\beta_{12} = g_{\text{core}}^{12} + g_{\text{elec}}^{12} \quad (43)$$

where, g_{core}^{12} and g_{elec}^{12} are the free energy contributions associated with the interactions between the hydrophobic moieties of surfactants 1 and 2 in the micellar core and the electrostatic interactions between the charged hydrophilic moieties of surfactants 1 and 2, respectively. In case of binary mixtures of hydrocarbon-based surfactants $g_{\text{core}}^{12} = 0$, and equation (43) can then be written as

$$\beta_{12} = g_{\text{elec}}^{12} = -K_{\text{elec}} (Z_1 - Z_2)^2 \quad (44)$$

where K_{elec} is a numerical prefactor which can be evaluated from electrostatic theories. For the pairs with similar charges *e.g.*, for nonionic-nonionic, cationic-cationic, and anionic-anionic combinations $\beta_{12} = 0$. For ionic surfactant, g_{elec}^{12} is obtained from the following equation,

$$g_{\text{elec}}^{12} = 2kT \left[\ln(s/2 + (1 + (s/2)^2)^{1/2}) - \{(1 + (s/2)^2)^{1/2} - 1\} / (s/2) \right] - 2kT \left[(4/s\kappa R) \ln((1 + (1 + (s/2)^2)^{1/2}) / 2) \right] \quad (45)$$

where, $s = 4\pi Ze^2/\varepsilon akT\kappa$ and $\kappa^{-1} = (8\pi C_0 e^2 Z^2/\varepsilon kT)^{1/2}$

C_0 is the bulk ionic concentration, a is the available surface area per charge, ε is the dielectric constant of the solvent, Z is the valence of the ionic surfactant, s is a convenient dimensionless parameter, and κ^{-1} is the well known Debye screening length. The factor g_{elec}^{12} can also be given by

$$g_{elec}^{12} = K_{elec} (Z_1 - Z_2)^2 (\alpha^*)^2 + 2((Z_1 - Z_2)Z_2\alpha^* + Z_2) \quad (46)$$

From Equations (45) and (46), K_{elec} is obtained following the recommended procedure of Sarmoria *et al.*, which, in turn, gives the value of β_{12} from Equation (44). Once the value of β_{12} is obtained, several other important parameters could be obtained¹³⁶⁻¹³⁹.

Micelle Formation in Non-aqueous Solvents

Surfactants are widely used both in industry and everyday life. Hence the properties of surfactant aqueous solutions have received considerable attention. The aggregation phenomenon of amphiphiles in non-aqueous media has been the scope of many researchers due to increasing use of these materials in applications which require water-free or water-poor media^{140, 141}. The normal micelles are essentially formed in aqueous medium. In nonpolar solvent media *viz.*, cyclohexane, carbon tetrachloride, hydrocarbons (heptane, octane, decane etc.) normal micelle is not formed. Instead, a reverse orientation of the surfactants takes place in the assembled units, the head groups remain directed towards the interior whereas the tails are projected towards the nonpolar continuum. This is the generalized state of a reverse micelle (Figure 12). Generally, a trace amount of a polar solvent *e.g.*, water is required for easy and stable formation of reverse micelle.

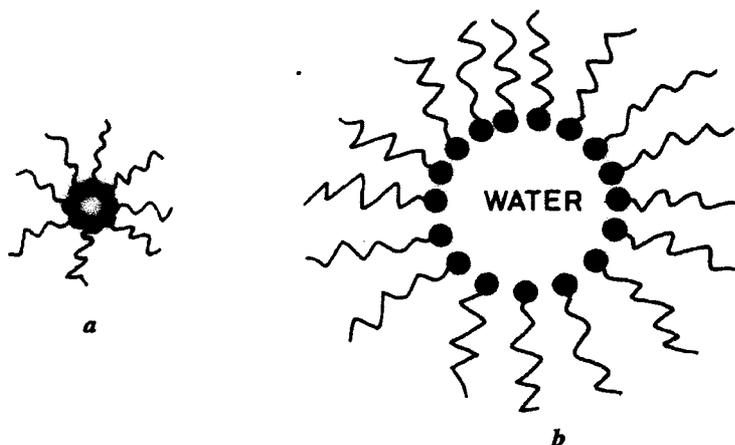


Figure 12. Schematic representation of reverse micelles (a) in absence of water
(b) in presence of water¹⁴².

The reason for micelle formation in organic solvents is somewhat different from that in aqueous solution. The main cause of micellization is the energy change due to dipole-dipole interactions between the polar head groups of the surfactant molecules. In general, aggregation numbers are small in organic media, often not exceeding five monomers per micelle. Instead of a spherical micelle, a lamellar micellar model comprising of a double layer of oriented molecules placed end-to-end and tail-to-tail with sheets of solvent molecules between the surfactant layers was proposed by Kertes and Gutmann¹⁴³. Lamellar aggregation has been reported for metal carboxylates in hydrocarbons¹⁴⁴⁻¹⁴⁷, alkylbenzene and dialkylnaphthalene sulphonates^{148, 149}, sulphosuccinates¹⁴⁸ and lecithin in benzene¹⁴⁹⁻¹⁵¹.

Ruckenstein and Nagarajan¹⁵² from a consideration of the physical factors controlling aggregation, have argued against the existence of a *cmc* in these systems. However, Jean et al.^{153, 154} by positron annihilation technique have confirmed micelle formation for Aerosol OT (sodium 2-ethyhexyl sulfosuccinate) and dodecylammonium propionate in benzene and cyclohexane, and the *cmc* values obtained agreed well with the *cmc* values determined by light-scattering and vapour-pressure depression¹⁵⁵, dye absorption techniques¹⁵⁶, dielectric increment measurements¹⁵⁷ and ¹H nmr^{158, 159}.

Recently, other than these nonpolar solvents, aggregation of several amphiphiles in non-aqueous polar solvents has received considerable attention¹⁶⁰⁻¹⁷¹. Micelle or liquid crystal formation has been reported in solvents such as ethylene

glycol^{168, 169}, glycerol¹⁶⁰, formamide¹⁶¹⁻¹⁶³, and hydrazine^{164, 165}. All these solvents have high cohesive energies and dielectric constants and considerable hydrogen-bonding ability. Evans *et al.*¹⁷² have suggested that the hydrogen-bonding ability of a solvent is a prerequisite for micellization to occur. However, micellization of several amphiphiles has been reported¹⁷³⁻¹⁷⁵ in pure solvents such as acetonitrile, dimethyl sulfoxide and acetone where hydrogen-bonding ability is either nonexistent or very minimal.

In this thesis, we have devoted our attention to the micellization behavior of some anionic and cationic surfactants in aqueous and non-aqueous media with special attention to mixed micellization using different experimental techniques.

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