

Colloidal Materials: Part V

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1.6.1 Classification of surfactants

- ♦ One of the methods to classify the surfactants is by the type of head-groups they possess. As per this method, the surfactants are classified into four types: anionic, cationic, zwitterionic and nonionic.
- ♦ The surfactants can also be classified based upon their origin, structural features, or behavior in solution, e.g., gemini surfactants and biosurfactants. These surfactants can be any of the anionic, cationic, zwitterionic or nonionic types.

1.6.1.1 Anionic surfactants

- ♦ The head-group of an anionic surfactant is negatively charged, which is electrically neutralized by an alkali metal cation. The soaps ($\text{RCOO}^- \text{Na}^+$), alkyl sulfates ($\text{RSO}_4^- \text{Na}^+$) and alkyl benzene sulfonates ($\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$) are the well known examples of the anionic surfactants.
- ♦ These surfactants readily adsorb on the positively charged surfaces.
- ♦ The anionic surfactants are the most widely used surfactants in industrial practices. The linear alkyl benzene sulfonates have the highest consumption. Some of the anionic surfactants (e.g., salts of fatty acids) are precipitated from the aqueous solution in presence of salts containing Ca^{+2} and Al^{+3} ions. Therefore, their use may be restricted in certain media (e.g., hard water).
- ♦ The calcium and magnesium salts of alkyl benzene sulfonates are soluble in water. Therefore, they are much less sensitive to hard water.

1.6.1.2 Cationic surfactants

- ♦ The head-group of a cationic surfactant has a positive charge. The cationic surfactants are useful for adsorption on negatively charged surfaces.
- ♦ Some of the common uses of the cationic surfactants are in ore flotation, textile industries, pesticide applications, adhesion, corrosion inhibition and preparation of cosmetics.

- ◆ Most of the cationic surfactants have good stability in a wide range of pH. The relatively less use of cationic surfactants in industry is due to their rather poor detergency, lack of suspending power for carbon, and higher cost.
- ◆ Some well known cationic surfactants are, long chain amines ($\text{RNH}_3^+ \text{X}^-$), quaternary ammonium salts $[\text{RN}(\text{CH}_3)_3^+ \text{X}^-]$ and quaternary salts of polyethylene oxide-amine derivatives $[\text{RN}(\text{CH}_3)\{(\text{C}_2\text{H}_4\text{O})_x\text{H}\}_2^+ \text{Cl}^-]$.

1.6.1.3 Zwitterionic surfactants

- ◆ These surfactants have both positive and negative charges on the surface-active part of the molecule. The long chain amino acids ($\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$) are the well known examples of the zwitterionic surfactants.
- ◆ The main advantage of these surfactants is that they are compatible with both anionic and cationic surfactants due to the presence of both positive and negative charges. They are less irritating to eye or skin. Therefore, they find wide use in cosmetics. They are also used as fabric softeners and bactericides.
- ◆ Most of these surfactants are sensitive to pH. They show the properties of anionic surfactants at high pH whereas they behave as cationic surfactants at low pH. The sulfobetaine-type of surfactants $[\text{RN}^+(\text{CH}_3)_2(\text{CH}_2)_x\text{SO}_3^-]$ remain zwitterionic in a wide range of pH.

1.6.1.4 Nonionic surfactants

- ◆ The nonionic surfactants are second most widely used surfactants in the industry. They do not have any significant electric charge on their surface-active part. Therefore, there is very little or no electrical interaction between the head-groups. These surfactants are stable in presence of electrolytes.
- ◆ They are compatible with most other types of surfactants. These surfactants disperse carbon well. Therefore, they have a large number of industrial uses. Most of the nonionic surfactants are available in the form of viscous liquids. They usually generate less foam than the ionic surfactants.

- ◆ Some nonionic surfactants are virtually insoluble in water, but soluble in organic solvents. However, some nonionics are soluble both in water and organic liquids, although the extent of solubility differs. The solubility depends on the structure of the surfactant molecules.
- ◆ The alkyl phenol ethoxylate $[\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}]$ category of surfactants is widely used in emulsions, paints and cosmetics. The alcohol ethoxylates $[\text{R}(\text{OC}_2\text{H}_4)_x\text{OH}]$ are biodegradable. They are quite resistant to hard water. Therefore, in the applications involving saline media where the anionic surfactants are salted out of the solution, these surfactants find extensive use.
- ◆ The polyoxypropylene glycols are used in a wide range of molecular weights (e.g., 1000 – 30000). They are mainly used as dispersing agents for pigments in paints, foam-control agents and for removing scales of boilers. The polyoxyethylene mercaptants $[\text{RS}(\text{C}_2\text{H}_4\text{O})_x\text{H}]$ are stable in hot and alkaline solutions. They are used in textile detergents, metal cleaning and shampoos. They are also used with quaternary ammonium-type of cationic surfactants to enhance the effectiveness of the latter.
- ◆ The long chain esters of carboxylic acids have very good emulsifying properties. However, they are unstable to acid and alkali, especially under hot conditions.
- ◆ The edible sorbitol esters are used in food products such as ice creams, beverages, desserts and various confectionary products. These surfactants are also used in pharmaceutical products.
- ◆ The alkanolamines have good stability in the alkaline media. They are mainly used as laundry detergents, thickeners for liquid detergents, shampoos, rust inhibitors and fuel oil additives. The polyoxyethylene silicones are used as wetting agents.

1.6.1.5 Gemini surfactants

- ◆ These surfactants belong to a relatively new class of surfactants as compared to the conventional surfactants discussed before. They have two or three hydrophobic, and usually two hydrophilic groups, as illustrated in Fig. 1.6.1.

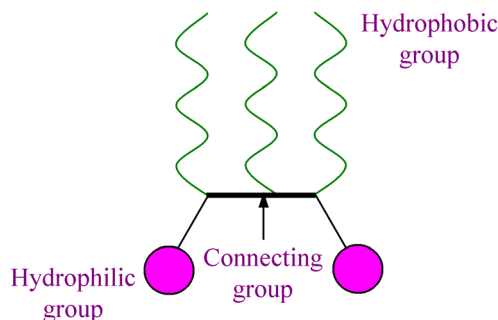


Fig. 1.6.1 Gemini surfactant.

- ◆ The hydrophobic groups are connected by a linkage that is close to the hydrophilic groups.
- ◆ The properties of these surfactants vary greatly depending upon the structure of these three parts of the molecule.
- ◆ The interfacial effects of these surfactants may be much stronger than the surfactants having a single hydrophilic and hydrophobic group. The gemini surfactants can have negative, positive or both types of charges. They can be nonionic as well. Since these surfactants have a large number of carbon atoms in their hydrophobic part, they show a penchant for adsorbing at the interface. However, at the same time, their solubility in water may be less. The hydrophilic groups prevent this difficulty. These surfactants require only a small amount to saturate the interface.

1.6.1.6 Biosurfactants

1.6.1.6.1 Advantages of biosurfactants

- ◆ Petrochemicals are often the first choice of the surfactant manufacturers because the surfactants can be produced at a low cost, the raw materials are easily available, and the performance of the surfactants is good.
- ◆ However, the major problem with many petrochemical-based surfactants is that they are not easily biodegradable. Sometimes toxic byproducts are formed during the manufacture of these surfactants.

- ◆ To avoid these problems, the biosurfactants are good alternatives. The biosurfactants are made of biological components such as carbohydrates. In recent times, they have found widespread use in petroleum engineering (such as oil recovery), food industries, pharmaceuticals, cosmetics and environmental pollution abatement.
- ◆ The protein-based surfactants have good prospects in the pharmaceutical formulations and personal-care products, where safety, mildness to skin, surface activity, antimicrobial activity and biodegradability are required.
- ◆ The main advantages of biosurfactants over the petroleum-based surfactants are their lower toxicity, biodegradable nature, and effectiveness at low as well as high temperatures. They are also usable in a wide range of pH and salinity of the medium.

1.6.1.6.2 Types of biosurfactants and their properties

- ◆ The low-molecular-weight biosurfactants are glycolipids. On the other hand, the high-molecular-weight biosurfactants are generally either polyanionic heteropolysaccharides or complexes containing both polysaccharides and proteins.
- ◆ Generally, biosurfactants are microbial metabolites. A variety of micro-organisms produce biosurfactants. Among the microbes, bacteria produce a majority of biosurfactants. The major types of biosurfactants produced by microorganisms are presented below.

(i) Glycolipids

- ◆ Trehalose mycolates and esters
- ◆ Mycolates of mono-, di-, and trisaccharide
- ◆ Sophorolipids
- ◆ Rhamnolipids

(ii) Fatty acids

(iii) Phospholipids

(iv) Lipopeptides and Lipoproteins

- ◆ Gramicidins
- ◆ Polymyxins
- ◆ Ornithine–lipid
- ◆ Cerilipin
- ◆ Lysin–lipid
- ◆ Surfactin, subtilysin
- ◆ Peptide–lipid

(v) Polymeric surfactants

- ◆ Lipoheteropolysaccharide
- ◆ Heteropolysaccharide
- ◆ Polysaccharide–protein
- ◆ Manno-protein
- ◆ Carbohydrate–protein
- ◆ Mannan–lipid complex
- ◆ Mannose/erythrose–lipid
- ◆ Carbohydrate–protein–lipid complex

(vi) Particulate biosurfactants

- ◆ Membrane vesicles
- ◆ Fimbriae
- ◆ Whole cells

1.6.2 Formation of micelles

- ◆ One fundamental property of the surfactants is to adsorb at the interfaces. Surfactants have another very important property—the property of *self-assembly*.
- ◆ When sufficient amount of a surfactant is dissolved in water, the surfactant molecules form colloidal clusters. For many ionic surfactants, typically 40–100 surfactant molecules assemble to form such clusters. These are called *micelles*, and the process of formation of micelles is known as *micellization*.

- ◆ The number of surfactant molecules in a micelle is known as *aggregation number*. These clusters can have a wide variety of shape, such as spherical, cylindrical and lamellar, as shown in Fig. 1.6.2.

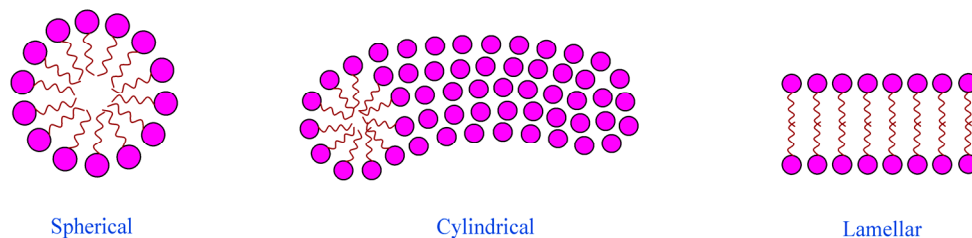


Fig. 1.6.2 Micelles of various types.

- ◆ The threshold concentration at which the formation of micelle begins is known as *critical micelle concentration (CMC)*. The CMC of some surfactants in water are given in Table 1.6.1.

Table 1.6.1 CMCs of surfactants

Surfactant	Formula	CMC (mol/m ³)
Cetyltrimethylammonium bromide	$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+ \text{Br}^-$	0.90
Sodium dodecyl sulfate	$\text{C}_{12}\text{H}_{25}\text{SO}_4^- \text{Na}^+$	8.10
Tween 20	$\text{C}_{58}\text{H}_{114}\text{O}_{26}$	0.05
Triton X-100	$\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_{9.5}$	0.20

- ◆ Several properties of surfactant solution show sharp change in the vicinity of CMC, such as surface tension, equivalent conductivity, osmotic pressure and turbidity, as shown in Fig. 1.6.3.

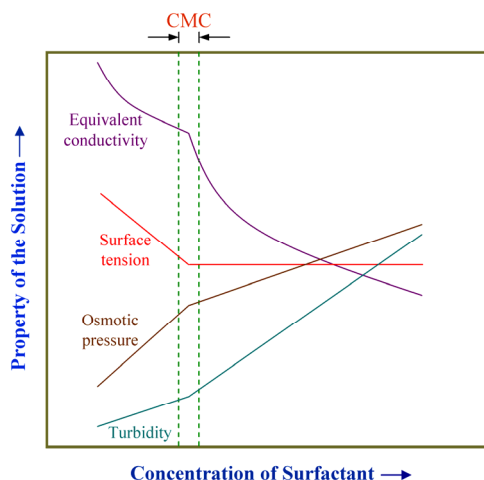


Fig. 1.6.3 Variation of properties of surfactant solution near the CMC.

- ◆ These variations can be explained as follows. Near the CMC, the surface is almost saturated by the adsorption of the surfactant molecules. Therefore, the surface tension ceases to decrease when the surfactant concentration is increased beyond the CMC. The equivalent conductivity of the solution decreases at the CMC owing to the lower mobility of the micelles as compared to the surfactant molecules. When the critical micelle concentration is approached, the slope of the osmotic pressure curve decreases and the slope of the turbidity curve increases due to the increase in the average molecular weight of the solute.
- ◆ The size and shape of the micelles depend on the properties of the solution such as the concentration of electrolyte and the pH of the solution. To illustrate, the aggregation number of sodium dodecyl sulfate micelle is ~ 80 , which increases to ~ 130 in 0.4 mol/m^3 NaCl solution. With the addition of electrolyte (such as NaCl), the critical micelle concentration of ionic surfactants decreases. The electrolytes mask the electrostatic repulsion between the ionic head-groups of the surfactant molecules. This favors more adsorption of the surfactant molecules at the interface, which causes the reduction in CMC. Sometimes, increase in pH favors ionization. If the charge density increases by changing the pH, the CMC may increase.
- ◆ The aggregation number increases with increasing length of the hydrocarbon chains of the surfactant molecules. For example, the aggregation number of

decyltrimethylammonium bromide is ~ 36 whereas, the same for tetradecyltrimethylammonium bromide is ~ 75 . The critical micelle concentration decreases with the increasing chain length. The CMC also depends on the size of the hydrophilic group. As the size of the hydrophilic group gets larger, the repulsion between them increases.

- ◆ The shape of some micelles changes with surfactant concentration. Some micelles change their structure from spherical to cylindrical to lamellar with increasing surfactant concentration. This transformation can be facilitated by electrolytes also.
- ◆ The mechanism of aggregation of surfactant molecules is believed to be reversible. The surfactant molecules join and leave the micelle very rapidly ($\sim 10^{-6}$ s). The counterions at the surface of the micelles exchange at even faster rates. The water molecules which are bound to the micelles are highly mobile as well. The typical lifetime of water molecules in the micelle is about 10^{-8} s.

1.6.3 Structure of micelles

- ◆ The structures of the micelles of anionic and cationic surfactants are essentially the same. The micelles of nonionic surfactants are sometimes very large, and the number of surfactant molecules in these clusters can be much greater than 100.
- ◆ The diameter of the cylindrical micelles is of the order of a few nanometers. However, their length can be large. For example, the micelles of an ethoxylated C_{16} alcohol and ethylene oxide were found have diameter in the range of 3–8 nm, but their length was ~ 1000 nm. The micelles of nonionic surfactants may have several hundreds of molecules.
- ◆ McBain (1913) proposed that the micelles can have lamellar and spherical shapes. Hartley proposed the ‘core model’ in 1936, in which a liquid-like hydrocarbon core is surrounded by a hydrophilic surface layer, which is constituted by the head-groups of the surfactant molecules. The central core is mainly hydrocarbon.
- ◆ The hydrophilic head-groups of the surfactant molecules repel each other electrically whereas the hydrophobic groups attract each other by hydrophobic attraction. Therefore, two opposing forces act in the interfacial region: one tends

to increase and the other tends to decrease the head-group area. This is shown in Fig. 1.6.4.

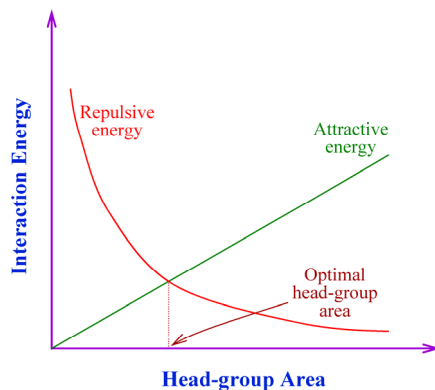


Fig. 1.6.4 Energy diagram for optimal head-group area.

- ◆ The optimal area is the area corresponding to the intersection of the two energy curves. When the surfactant molecules pack together to assume a geometrical structure, the relative size of the head-group and hydrophobic chain determines the size and shape of the micelle. The effects of hydration, repulsion between the ions and the effects of the counterion are also important in the packing of the molecules.

1.6.3.1 Packing parameter

- ◆ The structure of micelles is characterized by the 'packing parameter', defined as $v/(al)$, where v is the volume occupied by the hydrophobic group in the micellar core (i.e., the chain volume), l is the length of the hydrophobic group in the micellar core and a is the optimal (cross-sectional) area occupied by the hydrophilic group at the micelle-solution interface. These quantities are shown in Fig. 1.6.5.

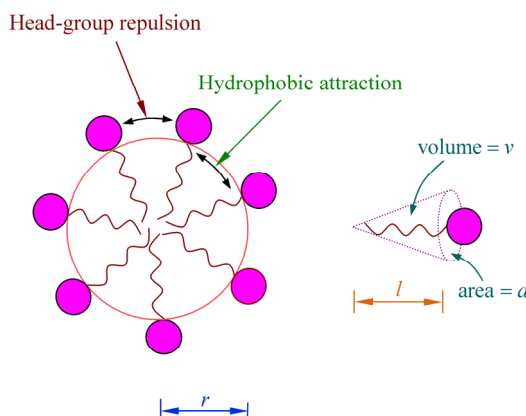


Fig. 1.6.5 Structural parameters of micelle.

- ♦ The magnitude of l is similar to the fully-extended molecular length of the hydrocarbon chains, but somewhat less. The optimal radius of the micelle (r) must not exceed l in order to maintain the liquid-like core of the micelle.

1.6.3.2 Tanford equations

- ♦ The values of v (in nm^3) and l (in nm) can be calculated from the following equations given by Tanford (1980).

$$v = 0.0274 + 0.0269n \quad (1.6.1)$$

$$l \leq 0.154 + 0.1265n \quad (1.6.2)$$

where n is the number of carbon atoms of the saturated hydrocarbon chain embedded in the core of the micelle. From Eqs. (1.6.1) and (1.6.2), we can observe that as n becomes large, the v/l ratio approaches 0.21 nm^2 . This defines the minimum cross-sectional area that a hydrocarbon chain can have. The maximum value of l ($\equiv l_{\text{max}}$) is given by the equality in Eq. (1.6.2). If the length of the chains extends beyond this limit significantly, their aggregation may not be considered liquid-like.

- ♦ The optimal area occupied by the hydrophilic group at the surface of the micelle (a) depends on the structure of the group, electrolyte concentration, pH and the

presence of any additive (such as alcohol) in the solution. For ionic surfactants, addition of electrolyte causes the value of a to reduce.

- ♦ The variation of the structure of the micelles with the packing parameter is illustrated in Table 1.6.2.

Table 1.6.2 Packing parameter and the shape of micelle

Packing parameter, $v/(al)$	Shape of the micelle
$0 - 1/3$	Spherical
$1/3 - 1/2$	Cylindrical
$1/2 - 1$	Lamellar
> 1	Reverse micelles

Example 1.6.1: The aggregation number of sodium dodecyl sulfate micelle in water is 80. Calculate the packing parameter, and predict the shape of the SDS micelles.

Solution: For SDS, the number of carbon atoms in the hydrophobic chain (n) is 12. From Eqs. (1.6.1) and (1.6.2) we get,

$$v = 0.3502 \text{ nm}^3$$

$$l_{\max} = 0.154 + 0.1265n = 1.672 \text{ nm}$$

Given, $N = 80$

The aggregation number is defined as,

$$N = \frac{4\pi r^3}{3v} \quad (\text{assuming the micelle to be spherical})$$

$$\therefore r = \left(\frac{3vN}{4\pi} \right)^{1/3} = \left(\frac{3 \times 0.3502 \times 80}{4 \times \pi} \right)^{1/3} = 1.884 \text{ nm}$$

$$\therefore r > l_{\max}$$

$$a = \frac{4\pi r^2}{N} = \frac{4 \times \pi \times (1.884)^2}{80} = 0.558 \text{ nm}^2$$

$$\therefore \frac{v}{al} = \frac{0.3502}{0.558 \times 1.672} = 0.375$$

This value is slightly higher than the upper limit of $v/(al)$ for the structure of the micelle to be spherical. Therefore, the SDS micelles will be non-spherical to some extent.

Example 1.6.2: The light scattering data from aqueous solutions of the cationic surfactant, dodecyltrimethylammonium bromide, are presented below.

c (kg/dm ³)	0.006	0.010	0.015	0.020	0.025	0.030
$\frac{H(c-c_{\text{CMC}})}{\tau} \times 10^4$ (kmol/kg)	0.83	1.07	1.63	2.02	2.35	2.76

where τ is the turbidity in excess of that of the solvent, c is the concentration of the surfactant and c_{CMC} is the critical micelle concentration. Calculate the molecular weight of the micelle and the aggregation number from these data. Given: $c_{\text{CMC}} = 4.4 \text{ kg/m}^3$.

Solution: The turbidity below the CMC is essentially the same as that for the solvent. The light scattering centers are the micelles of the surfactant. Let us write the Debye equation as,

$$\frac{H(c-c_{\text{CMC}})}{\tau} = \frac{1}{M} + 2B(c-c_{\text{CMC}})$$

where M is the weight-average molecular weight of the micelle and B is the second virial coefficient. The surfactant solution of concentration c is considered to consist of monomers of concentration c_{CMC} , and micelles of concentration $(c-c_{\text{CMC}})$. The solution at the CMC is designated as the solvent. The plot is shown in Fig. 1.6.6. The intercept is,

$$\frac{1}{M} = 6.93 \times 10^{-5} \text{ kmol/kg}$$

Therefore, the molecular weight is,

$$M = 14430 \text{ kg/kmol}$$

The molecular formula of dodecyltrimethylammonium bromide is $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{NBr}$. The molecular weight, therefore, is 308. Therefore, the aggregation number of the micelle is 47.

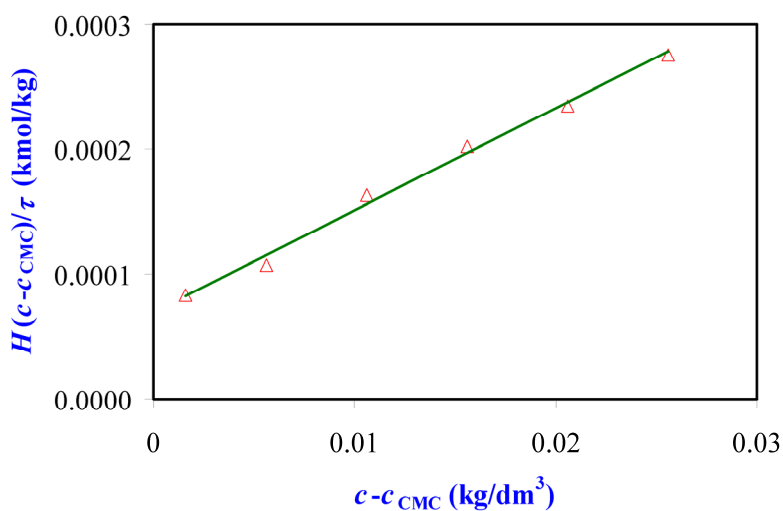


Fig. 1.6.6 Determination of molecular weight of micelle from Debye plot.

1.6.4 Reverse micelles

- ◆ When the value of the packing parameter exceeds unity, some surfactants form *reverse micelles* in non-polar media. The surfactant molecules assemble in structures in which the head-groups are oriented inwards and the hydrophobic groups are oriented towards the solvent (Fig. 1.6.7).

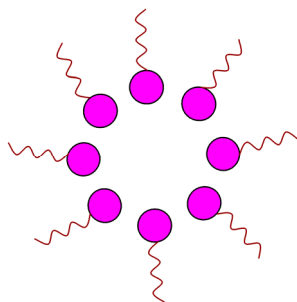


Fig. 1.6.7 Reverse micelle.

- ♦ The aggregation number in reverse micelles is usually much smaller than the aggregation number in the aqueous micelles. The negative enthalpy change during micellization is believed to be an important stabilizing factor for the reverse micelles.
- ♦ Surfactants soluble in organic liquids can form reverse micelles. There are some surfactants, such as Aerosol OT, which can form normal as well as reverse micelles.

1.6.5 Applications of micelles

- ♦ The micelles present in water can dissolve organic molecules. Conversely, the reverse micelles can solubilize water molecules. The liquid dissolves in the micelle. This depends on the chemical nature of the liquid as well as the surfactant. The extent to which a liquid can be solubilized by the micelles depends on the concentration of the surfactant in the solution. The amount of surfactant necessary to solubilize an organic liquid is large.
- ♦ Micelles have been used as reaction-vessels for the manufacture of nanoparticles. The nanoparticles formed inside the micelles are organized inside them. Metal nanoparticles (e.g., gold, silver and platinum) have been synthesized by this technique. The micelles created from block copolymers such as poly styrene–ethylene oxide have been used to generate well-ordered compartments.
- ♦ Block copolymer micelles can act like water-soluble biocompatible nanocontainers with great potential for delivering hydrophobic drugs.
- ♦ Reactions of organic compounds are sometimes significantly enhanced in the aqueous micellar solutions of ionic surfactants. This is known as *micellar catalysis*.
- ♦ Micelles have also been used to remove pollutants from wastewater. The pollutant molecules are trapped inside the micelles. These micelles are then separated by ultrafiltration. This method is known as *micelle-enhanced ultrafiltration* (MEUF).

1.6.6 Bilayers, liposomes and vesicles

- ◆ When the effective areas of the hydrophilic and hydrophobic groups are nearly equal, the micelles can take up lamellar structure. A well-known example of this type of shape is *lipid bilayer*, which is made of double-chained lipid. The lamellar micelles have a tendency to form multilayers.
- ◆ The *vesicles* are lamellar micelles bent around and joined-up in a sphere [Fig. 1.6.8 (a)]. An aqueous solution core remains inside the sphere. Formation of the closed bilayer of the vesicles is favorable because the energetically unfavorable edges of the planar structure are eliminated, and a finite number of surfactant molecules aggregate. Usually surfactants having two alkyl chains (e.g., the double-chained lipids) with large head-group areas form vesicles. A mixture of single-chain anionic and cationic surfactants of similar hydrophobic size can also form vesicles. It is likely that a two-tailed salt having a large hydrophobic part is formed from these surfactants, which encourages the formation of the vesicle.
- ◆ Concentric spheres of vesicles are termed *liposomes* [Fig. 1.6.8 (b)]. The interactions in the bilayers of vesicles and liposomes are different. It is believed that the hydration force imparts them stability. The liposomes have been used as ‘containers’ for drugs and genetic materials.

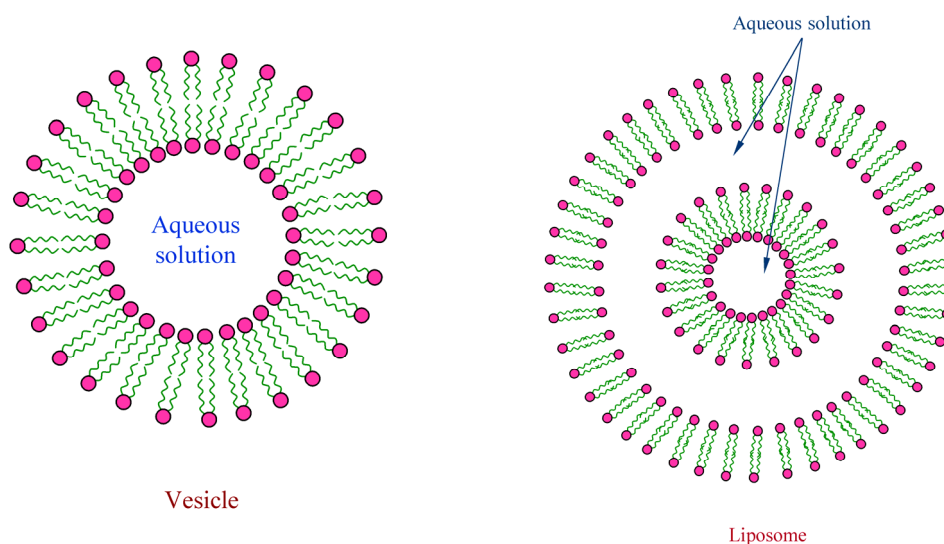


Fig. 1.6.8 Self-assembled structures: (a) vesicle, and (b) liposome.

- ◆ Biologists have used the vesicles as models for the cell membranes. It is believed that the vesicles represent the prototypes of early living cells. It has been demonstrated that certain lipids as well as synthetic surfactants can spontaneously self-assemble to form vesicles.

1.6.7 Thermodynamics of micellization

- ◆ Let us consider a surfactant which is represented as S . If the surfactant is ionic, it represents the surface-active part. The effects associated with counterions (e.g., their binding effects) are not considered in the following derivation for simplicity. When the micelle (S_N) forms, the clustering can be represented by the following reaction.



where N is the aggregation number. The aggregation number actually has a statistical distribution rather than a single value as used here.

- ◆ The reaction represented by Eq. (1.6.3) is reversible. The equilibrium constant for this reaction is given by,

$$K = \frac{a_{\text{micelle}}}{a_S^N} \quad (1.6.4)$$

where a represents activity in Eq. (1.6.4), expressed in terms of mole fraction. The standard Gibbs free energy change for micelle formation per mole of surfactant is given by,

$$\Delta \bar{G}^0 = -\frac{RT \ln K}{N} = -\frac{RT}{N} \ln a_{\text{micelle}} + RT \ln a_S \quad (1.6.5)$$

- ◆ At the critical micelle concentration, $a_S = a_{\text{CMC}}$. Since N is large, Eq. (1.6.5) becomes,

$$\Delta \bar{G}^0 \approx RT \ln a_{\text{CMC}} \quad (1.6.6)$$

- ◆ The standard Gibbs free energy change due to micellization can be calculated from Eq. (1.6.6). The activity is expressed as the product of mole fraction and activity coefficient. For most surfactants, the critical micelle concentration is

small ($< 1 \text{ mol/m}^3$). Setting the activity coefficient to unity under the assumption of ideal behavior of the surfactant solution at CMC, Eq. (1.6.6) becomes,

$$\Delta \bar{G}^0 \approx RT \ln x_{\text{CMC}} \quad (1.6.7)$$

where x_{CMC} is the mole fraction of surfactant in the solution at CMC. The experimentally determined value of CMC (expressed as mole fraction) can be put in Eq. (1.6.7) to calculate $\Delta \bar{G}^0$.

1.6.8 Krafft point and cloud point

- ◆ The solubility of the surfactant molecules in water decreases with increasing length of the hydrophobic part, and the solubility increases if the hydrophilic part is more soluble. The solubility of surfactant is also dependent on temperature. The solubility of ionic surfactants increases very rapidly after a temperature, termed *Krafft point*.
- ◆ At this temperature, the micelles are formed, and the solubility is significantly increased. This temperature is important in industrial preparations, especially where concentrated surfactant solutions are required. The Krafft temperature increases with the increasing number of carbon atoms in the hydrophobic part.
- ◆ The Krafft point decreases linearly with the logarithm of CMC for many anionic surfactants. It is strongly dependent on the addition of electrolyte, the head-group and the counterion. Electrolytes usually raise the Krafft point. There is no general trend for the dependence on counterions. However, the Krafft point is typically much higher in presence of divalent counterions than monovalent counterions. For alkali alkanoates, Krafft point increases as the atomic number of the counterion decreases. The opposite trend is observed for alkali sulfates or sulfonates. For cationic surfactants, the Krafft point is usually higher for bromides than chlorides, and still higher for the iodides. The variation of Krafft point with the number of carbon atoms in the alkyl chain is shown in Fig. 1.6.9 (a).
- ◆ The solubility of some nonionic surfactants (such as the ethoxylates) decreases dramatically above a certain temperature. This temperature is termed *cloud point*.

These surfactants are quite soluble at the low temperatures (273–278 K). However, they come out of solution upon heating.

- ◆ These surfactants dissolve in water by hydrogen bonding. With increasing temperature, the hydrogen bonds disrupt. This causes reduction in solubility. Cloud point decreases with the increasing chain length of the hydrophobic part. The variation of cloud point with the number of oxyethylene units is depicted in Fig. 1.6.9 (b).

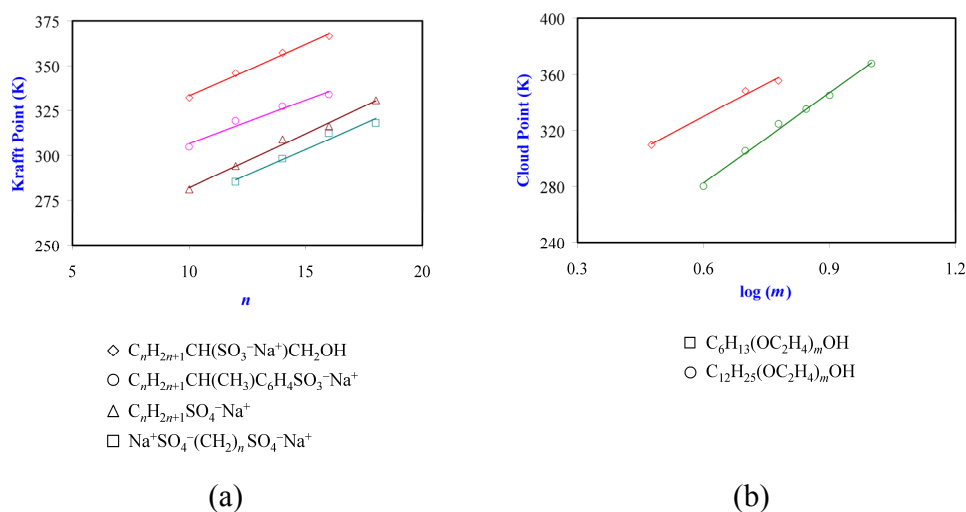


Fig. 1.6.9 (a) Variation of Krafft point with the number of carbon atoms in the alkyl chain, and (b) variation of cloud point with the number of oxyethylene units (source: T. Gu and J. Sjöblom, *Colloids Surf.*, **64**, 39, 1992; adapted by permission from Elsevier Ltd., © 1992).

1.6.9 Liquid crystals

- ◆ At the critical micelle solution (CMC), the solution contains a mixture of the micelles and the monomer at the concentration equal to the CMC. The micelles can have various shapes, as discussed in Section 1.6.3. When there is sufficient number of micelles in the solution, they start to pack together in a number of geometric arrangements, depending upon the shape of the individual micelles. These packed-arrangements are known as *liquid crystals*.
- ◆ The liquid crystalline phases are also known as *lyotropic mesomorphs* and *lyotropic mesophases*. The reverse micelles also can form liquid crystals.

- ◆ The liquid crystals are ordered like solid crystals, but they are mobile like liquids. The spherical micelles pack into cubic liquid crystals, cylindrical micelles form hexagonal liquid crystals, and lamellar micelles form lamellar liquid crystals.
- ◆ With increasing surfactant concentration, some cylindrical micelles become branched and interconnected leading to the formation of a bicontinuous liquid crystalline phase (see Fig. 1.6.10). The hexagonal phase appears at a lower surfactant concentration than that for the lamellar phase. The usual sequence of the phases is: micellar $\rightarrow$ hexagonal $\rightarrow$ lamellar.
- ◆ In between the changes from one phase to another, cubic phases can be detected. The hexagonal and lamellar phases are optically anisotropic. They can be detected under polarizing microscope. The cubic phase is isotropic. It can be identified by using dyes.
- ◆ Because of the ordered arrangement of the molecules in the liquid crystals, the viscosity of the solution increases considerably. The hexagonal phases are more viscous than the lamellar phases. The cubic liquid crystalline phases formed from bicontinuous structures and spherical micelles at high surfactant concentrations are high-viscosity gels. They are useful in cosmetic and pharmaceutical industries.

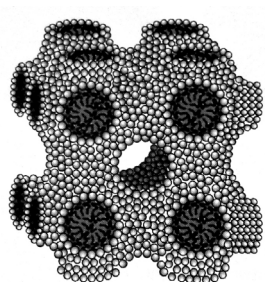


Fig. 1.6.10 Bicontinuous liquid crystal (Source: J. C. Berg, *An Introduction to Interfaces and Colloids*, World Scientific, Singapore, 2010; reproduced by permission from World Scientific Publishers, © 2010).

1.6.10 Hydrophilic–lipophilic balance (HLB)

- ♦ A major commercial use of the surfactants is to formulate emulsion-stabilizing agents, or *emulsifiers*. Emulsions can be divided into two types: oil-in-water (O/W) emulsions, and water-in-oil (W/O) emulsions. In the oil-in-water type of emulsions, oil droplets are dispersed in the continuous aqueous phase whereas, in water-in-oil type of emulsions, the aqueous phase is dispersed in the continuous oil phase.
- ♦ Some surfactants stabilize the O/W emulsions whereas the other surfactants are more efficient in stabilizing the W/O emulsions. A rule of thumb is that the most stable emulsion is formed when the surfactant has higher solubility in the continuous phase.
- ♦ Therefore, according to this rule, a water-soluble surfactant should stabilize oil-in-water emulsions more than water-in-oil emulsions, and the reverse is expected for a surfactant that is soluble in oil. This rule is known as *Bancroft's rule*.
- ♦ Griffin (1949) developed a method to correlate the structural properties of the surfactants with their ability to act as emulsifiers. This method is known as *hydrophilic–lipophilic balance (HLB) method*.
- ♦ The solubility of surfactants in water varies depending on their HLB value, as shown in Table 1.6.3.

Table 1.6.3 HLB values and types of emulsion formed

Range of HLB value	Solubility in water	Emulsion type
1–4	Insoluble	Water-in-oil
4–7	Poor unstable dispersion	Water-in-oil
7–9	Stable opaque dispersion	–
10–13	Hazy solution	Oil-in-water
13 and higher	Clear solution	Oil-in-water

- ♦ As the name suggests, the balance between the hydrophilic and lipophilic parts of the surfactant molecule is important in this method. Values have been assigned to

these parts for various surfactants. A group-number method is used for calculating the HLB value of a surfactant from its chemical formula.

$$\text{HLB} = \Sigma (\text{hydrophilic group-numbers}) - \Sigma (\text{group-number per } -\text{CH}_2- \text{ group}) + 7 \quad (1.6.8)$$

- ◆ The group-numbers for various hydrophilic and lipophilic groups are presented in Table 1.6.4.

Table 1.6.4 Groups numbers for calculation of HLB

Type of group	Group	Group-number
Hydrophilic	$-\text{SO}_4^- \text{Na}^+$	38.7
	$-\text{COO}^- \text{K}^+$	21.1
	$-\text{COO}^- \text{Na}^+$	19.1
	Sulfonate	11.0
	-N (tertiary amine)	9.4
	Ester (sorbitan ring)	6.8
	Ester (free)	2.4
	$-\text{COOH}$	2.1
	$-\text{OH}$ (free)	1.9
	$-\text{O}-$	1.3
	$-\text{OH}$ (sorbitan ring)	0.5
Lipophilic	$-\text{CH}_3$	0.475
	$-\text{CH}_2-$	
	$-\text{CH}=\text{CH}-$	
	$-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-)$	0.15

Exercise

Exercise 1.6.1: Using the Tanford equations, calculate the minimum cross-sectional area for a hydrocarbon chain.

Exercise 1.6.2: The aggregation number of the surfactant $C_{10}H_{21}N(CH_3)_3Br$ has been reported to be 36. Can its micelle be spherical?

Exercise 1.6.3: The critical micelle concentration of cetyltrimethylammonium bromide is 1 mol/m^3 . Estimate the standard Gibbs free energy change due to micellization.

Exercise 1.6.4: Calculate the HLB value of *n*-propanol using the appropriate group-numbers.

Exercise 1.6.5: Answer the following questions clearly.

- (a) Give two examples of cationic, anionic and surfactants. Explain the salient features of a zwitterionic surfactant.
- (b) Explain the main features of a gemini surfactant. What is the reason behind their strong surface activity?
- (c) What are the advantages of the biosurfactants?
- (d) Explain what you understand by a micelle. What is micellization? What is aggregation number?
- (e) What is critical micelle concentration? Explain the effects of surfactant chain length and concentration of electrolyte on critical micelle concentration.
- (f) What factors govern the shape of a micelle? What are the commonly-observed shapes of the micelles?
- (g) Explain what you understand by vesicle and liposome. What are their uses?
- (h) Explain what you understand by reverse micelle. How does it differ from a normal micelle?
- (i) Explain what you understand by Krafft point. On what factors does the Krafft point depend?

- (j) Explain what you understand by cloud point. How does the cloud point of a surfactant vary with its chain length?
- (k) Explain the HLB concept of classification of surfactants.
- (l) If a surfactant has $HLB = 3$, what type of emulsion would you expect it to form?

Suggested reading

Textbooks

- ◆ D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth-Heinemann, Oxford, 1992, Chapter 4.
- ◆ M. J. Rosen, *Surfactants and Interfacial Phenomena*, John Wiley, New Jersey, 2004, Chapters 1 & 3.
- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 3.

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- ◆ G. J. M. Koper, *An Introduction to Interfacial Engineering*, VSSD, Delft, 2009, Chapter 3.
- ◆ J. C. Berg, *An Introduction to Interfaces and Colloids: The Bridge to Nanoscience*, World Scientific, Singapore, 2010, Chapter 3.
- ◆ J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1997, Chapters 16 & 17.
- ◆ R. J. Stokes and D. F. Evans, *Fundamentals of Interfacial Engineering*, Wiley-VCH, New York, 1997, Chapter 5.

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- ◆ H. Kunieda, K. Aramaki, T. Izawa, M. H. Kabir, K. Sakamoto and K. Watanabe, *J. Oleo Sci.*, **52**, 429 (2003).
- ◆ J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc. Faraday Trans. II*, **72**, 1525 (1976).
- ◆ K. Fontell, *Adv. Colloid Interface Sci.*, **41**, 127 (1992).
- ◆ K. Giribabu, M. L. N. Reddy, and P. Ghosh, *Chem. Eng. Commun.*, **195**, 336 (2008).
- ◆ T. Gu and J. Sjöblom, *Colloids Surf.*, **64**, 39 (1992).
- ◆ W. C. Griffin, *J. Soc. Cosmetic Chem.*, **1**, 311 (1949).