Chapter 1

Introduction
1.1 Surfactants

A surfactant (a contraction of the 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 of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). A surfactant molecule has a polar charged head group (non-polar in case of nonionic surfactants) and a long hydrophilic alkyl chain (tail)[Mittal, 1979; Myers, 1988; Rosen, 1989].

The applications of surfactants in industry area are quite diverse and have a great practical importance. Surfactants may be applied to advantage in the production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry products, petroleum, mineral ores, fuel additives and lubricants, paints, coatings and adhesives, and in photographic films. They can also be found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental, health, and safety applications [Schramm et al. , 2003]. Surfactants have even been the subject of investigation into the origins of life, meteorites containing lipid-like compounds have been found to assemble into boundary membranes and may be an interstellar prebiotic earth source of cell-membrane material [Deamer and Pashley, 1989]. There has been a continuous increase in the demands for the high performance surfactants, and according to the applications where the surfactants are to be utilized, novel surfactants have been successfully designed and developed. Anionic surfactants are the major class of surfactants used in various applications.

One of the most exciting developments in the field of surfactant chemistry is the emergence of the Gemini surfactants in the late 1980s and early 1990s. The term Gemini surfactant, coined by Menger [Menger and Littau, 1991], has become accepted in the surfactant literature for describing dimeric surfactants. “Gemini Surfactant” is a name assigned to a family of synthetic amphiphiles possessing, in sequence, a long hydrocarbon chain, an ionic group, a spacer, a second ionic group, and another hydrocarbon tail [Menger and Littau, 1991; Menger and Littau, 1993]. Gemini surfactants possess a number of superior properties when compared to conventional single-headed,
single-tailed surfactants, the Geminis tending to exhibit lower cmc values (by about an order of magnitude), increased surface activity ($C_{20}$) and lower surface tension at the cmc, enhanced solution properties such as hard-water tolerance, superior wetting times, and lower Krafft points. Given these performance advantages of Gemini surfactants one can anticipate their use in a myriad of surfactant applications (e.g., soil remediation, oil recovery, and commercial detergents), given a favourable cost/performance ratio. In the past two decades, gemini surfactants have attracted a lot of interest because of their very low critical micellar concentration (CMC) values and greater efficiency in reducing surface tension compared to conventional surfactants. Therefore, a small amount of Gemini surfactant can have dramatic effects in applications. These advantages led to a need to develop new varieties of gemini surfactants for industrial, agricultural, biological, or daily uses. Some gemini surfactants with specific performances have been introduced in markets as commercial products, individually or blended with other surfactants. Many patents cover the manufacture and application of anionic, cationic, zwitterionic, and nonionic gemini surfactants [Zana and Xia, 2005]. Gemini surfactants possess excellent solubilization, wetting, specific rheological and aggregation properties [Zana and Talmon, 1991; Zana and Levy, 1997; Zhu et al., 1991; Frindi et al., 1994; Alami et al., 1994; Alami et al., 1993; Zana et al., 1991; Camesano and Nagarajan, 2000]. Geminis can also be used as effective bactericidal agents, dispersants, anti foaming agents. An important feature of these surfactants is the ability to design their physicochemical properties, supra molecular structure and biodegradability by modifying the nature and size of the spacer moieties and alkyl chains [Prizomic, 2005]. A block diagram of conventional surfactant and gemini surfactant is depicted in Figure 1.1.
1.1.1 Classification of Surfactants

The hydrophobic group in a surfactant is generally a long-chain hydrocarbon group, although there are examples of using fluorinated or oxygenated hydrocarbon or siloxane chains. The hydrophilic or head group will be an ionic or highly polar group that imparts water solubility to the molecule. The most useful chemical classification of surface active agents is based on the nature of the hydrophilic or head group, with subgroups based on the nature of the hydrophobe or tail. The four basic classes of surfactants are defined as follows:

Anionic Surfactants

The hydrophilic is a negatively charged group such as carboxyl ($RCOO^- M^+$), sulfonate ($RSO_3^- M^+ M$), sulfate ($ROSO_3^- M^+$), or phosphate ($ROPO_3^- M^+$). For example, SLS:

![Sodium Lauryl Sulfate (SLS)](image)

Figure 1.1: Pictorial representation of Monomeric and Gemini Surfactants
Cationic Surfactants

The hydrophile bears a positive charge, as for example, the quaternary ammonium halides. For example, CTAB.

Nonionic Surfactants

The hydrophile has no charge, but derives its water solubility from highly polar groups such as polyoxyethylene, polyol groups including sugars. For example, Brij series;

Zwitterionic Surfactants

The molecule contains, or can potentially contain, both a negative charge and a positive charge, such as the sulfobetaines. For example; CAPB.

1.1.2 Classification of Gemini Surfactants

Classification of gemini surfactants can also be done in similar way the conventional monomeric surfactants are classified, i.e. on the basis of charge present on the head groups.
1.1.2.1 Anionic Gemini Surfactants

All anionic gemini surfactants have at least two hydrophobic chains and two anionic head groups (carboxylate, sulphonate, sulphate, phosphate etc.). The spacer can be polar (polyether) or nonpolar (aromatic or aliphatic), rigid (short aliphatic chain with double or triple bonds, benzene etc.) or flexible (methylene units). The spacer chain lengths can be short \( C_2 \) (methylene group), or long chain such as \( C_{12} \) or simply one oxygen atom. The very first anionic gemini (with bis phosphate head groups) surfactant was reported by authors Menger et.al [Menger and Littau, 1991], as shown in scheme-1.

\[ \text{Scheme 1: Anionic gemini surfactant with phosphate head groups} \]

1.1.2.2 Cationic Gemini Surfactants

In general, cationic gemini surfactants can be synthesized by heating under reflux alcoholic (ethanol) solutions of alkyldimethylamine and \( \alpha, \omega \)-alkylene-dihalide or of N,N,N,N-tetramethyl-\( \alpha, \omega \)-alkylenediamine and alkyl halide in order to achieve the quaternization of the amine. All cationic gemini surfactants have at least two hydrophobic chains (similar chain lengths) and two cationic head groups which are quaternary ammonium moieties.

\[ 2 \text{RN(CH}_3)_2 + X-Y-X \rightarrow \text{RN(CH}_3)_2-Y-\text{N(CH}_3)_2R \ 2X \]

\[ 2 \text{RX} + (\text{CH}_3)_2N-Y-N(\text{CH}_3)_2 \rightarrow \text{RN(CH}_3)_2-Y-\text{N(CH}_3)_2R \ 2X \]

R= alkyl chain; \( \ Y = -(\text{CH}_2)_n \ n=1,2; \quad X=\text{Br, Cl} \]
1.1.2.3 Zwitterionic Gemini Surfactants

There are relatively few reports concerning zwitterionic gemini surfactants and there is not enough data to establish the relationship between the structures of zwitterionic gemini surfactants and their properties. Due to the more advantages of zwitterionic surfactants over the ionic or nonionic surfactants such as excellent water solubility, low sensitivity to ionic strength, good biodegradation, and reduction in skin and eye irritation [Seredyuk and Holmberg, 2001; Boda et al., 2000], zwitterionic gemini surfactants have recently attracted increasing attention.

![Zwitterionic gemini surfactant](image)

R, R’ = C_{8}H_{17}, C_{18}H_{37}

Figure 1.2: Zwitterionic gemini surfactant
Ref.[Menger and Peresypkin, 2001]

1.1.2.4 Nonionic Gemini Surfactants

One of the other important type of gemini surfactants is nonionic gemini surfactants. There are very less articles reported on nonionic gemini surfactants compared to ionic gemini surfactants. In view of the importance of conventional nonionic surfactants, some new nonionic gemin surfactants are reported in literature. There are many articles reported wherein synthesis of nonionic geminis derived from natural sources is
described [Castro et al., 1997; Castro et al., 2002]. A gemini surfactant with sugar moiety and an ester linkage as a spacer group is shown in Figure 1.3.

![Figure 1.3: Nonionic gemini surfactant derived from sugar moiety](Ref.[Castro et al., 1997])

1.2 Interfacial Properties of Surfactants

A surfactant molecule tends to adsorb at an interface, and the orientation of the surfactant can be different for different surfactants owing to their structures.

The adsorption of surfactant at interface can be studied to determine;

A) The actual concentration of surfactant at the interface, which is a measure of how much of the interface has been covered by the surfactant; the performance of the surfactant in many interfacial processes (e.g., foaming, detergency, emulsification) depends on its concentration at the interface.

B) The orientation and packing of the surfactant at the interface, which can be correlated to the hydrophilic and hydrophobic nature of a surfactant

C) Adsorption kinetics, this determines the performance of a surfactant in applications involving such as high-speed wetting of surfaces.

D) The energy changes, $\Delta G$, $\Delta H$ and $\Delta S$, in the system, resulting from the adsorption, since these quantities provide information on the type and mechanism of any interactions involving the surfactant at the interface and the efficiency and effectiveness of its operation as a surface-active material.

The electrical double layer concept can be taken into consideration to study the process of adsorption of surfactant molecule.
1.2.1 Electrical Double Layer

At an interface there is always an unequal distribution of electrical charges between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side a net charge of the opposite sign, giving rise to potential across the interface and an electrical double layer. Interface charge originates via two processes,

1. Ionisation or dissociation of a functional group at the interface
2. Ionic adsorption onto the non charged surface from solution.

The net charge on one side of the interface must be balanced by an exactly equal net charge of opposite sign on the other side of the interface to maintain, overall electrical neutrality. An important aspect is the distribution of the counter ions in the solution around a charged surface, since this determines the rate of change in electrical potential with distance from a charged surface.

In the diffuse double layer model (Figure 1.4), the ionic atmosphere on the solution side is supposed to consist of two regions

a. A layer of strongly held counterions, adsorbed close to the charged surface on fixed sites due to strong electrostatic forces and
b. A diffuse layer of counterions, according to a balance between the electrical forces and those due to the random thermal motion

According to this model the electrical potential drops rapidly in the fixed portion (Stern layer) of the double layer and more gradually in the diffuse portion. Mathematical treatment of the diffuse layer gives the effective thickness, $k^{-1}$ of that layer. This is the distance from the charged surface into the solution within which the majority of electrical interactions are considered to occur. The effective thickness, often called the Debye screening length, is given by equation 1.1.

$$k^{-1} = \left( \frac{\varepsilon RT}{4\pi F^2 \sum CiZ_i^2} \right)$$

(1.1)

Where $\varepsilon$ is the static permitivity of a solution, $R$ is the gas constant, $T$ is the abso-
lute temperature, $F$ is the Faraday constant, $C_i$ and $Z_i$ are the molar concentration and valency of any ion in the solution phase.

Figure 1.4: Stern model of Electrical double layer
1.2.2 The Gibbs Adsorption Equation

A plot of surface (or interfacial) tension as a function of (equilibrium) concentration of surfactant in one of the liquid phases, is generally used to describe adsorption at these interfaces. From such a plot the amount of surfactant adsorbed per unit area of interface can readily be calculated by use of Gibbs adsorption equation. The Gibbs adsorption equation, in its most general form is fundamental to all adsorption processes where monolayers are formed [Rosen, 1989].

\[ d\gamma = - \sum \Gamma_i d\mu_i \]  \hspace{1cm} (1.2)

Where, \( d\gamma \) is the change in surface or interfacial tension of the solvent, \( \Gamma_i \) is the surface excess concentration of any component of the system and \( d\mu_i \) is the change in chemical potential of any component of the system.

At equilibrium between the interfacial and bulk phase concentrations, \( \mu d_i = RT d\ln a_i \); where \( a_i \) is the activity of any component in the bulk (liquid) phase, \( R \), is the gas constant and \( T \), absolute temperature. Thus,

\[ d\gamma = -RT \sum \Gamma_i d\ln a_i \]

\[ = -RT \sum \Gamma_i d\ln x_i f_i \]

\[ = -RT \sum \Gamma_i d(\ln x_i + \ln f_i) \]

Where \( x_i \) is the mole fraction of any component in the bulk phase and \( f_i \) it’s activity coefficient.

For solutions consisting of the solvent and only one solute,

\[ d\gamma = -RT (\Gamma_0 d\ln a_0 + \Gamma_1 d\ln a_1) \]

Where, subscripts 0 and 1 refers to the solvent and only one solute, respectively. For dilute solutions containing only one non-dissociating surface active solute, the activity
of the solvent and the activity coefficient of the solute can both be considered to be constant and the mole fraction of the solute $x_i$ may be replaced by its molar concentration $C_1$. Thus

\begin{equation}
d\gamma = -RT \Gamma_1 d\ln C_1
\end{equation}

\begin{equation}
= -2.303 RT \Gamma_1 d\log C_1
\end{equation}

which is the form in which the Gibbs equation is commonly used for solutions of nonionic surfactants containing no other materials. When $\gamma$ is in dyn/cm ($\text{ergs/cm}^2$) and $R = 8.31 \times 10^7 \text{ergs/mol/K}$, then $\Gamma_1$ is in $\text{mol/cm}^2$; when $\gamma$ is in mN/m ($= \text{mJ/m}^2$) and $R = 8.31 \text{J/mol/K}$, then $\Gamma_1$ is in $\text{mol/1000m}^2$.

For ionic surfactants,

\begin{equation}
d\gamma = -nRT \Gamma_1 d\ln C_1, = -2.303 nRT \Gamma_1 d\log C_1 \tag{1.3}
\end{equation}

where, $n$ is the number of solute species whose concentration at the interface changes with change in the value of $C_1$.

1.2.3 The Langmuir, Szyszkowski and Frumkin Equations

In addition to the Gibbs equation, three other equations have been suggested that correlate concentration of the surface active agent at the interface, surface or interfacial tension, and equilibrium concentration of the surfactant in a liquid phase. The Langmuir equation relates surface concentration with bulk concentration [Rosen, 1989].

\begin{equation}
\Gamma_1 = \frac{\Gamma_m C_1}{C_1 + a} \tag{1.4}
\end{equation}

The Surface excess concentration of the surfactant at interface ($\Gamma$) can be estimated from the plot of surface tension versus surfactant concentration (Figure 1.5) using Szyskowski equation. The Szyskowski equation, is the modified Gibbs adsorption
equation, can be represented as, equation 1.5

$$\gamma_0 - \gamma = \pi = -2.303 RT \Gamma_m \log \left( \frac{C_1}{a} + 1 \right)$$  \hspace{1cm} (1.5)

Where $\gamma_0$ is the surface tension of the solvent and $\pi$ is the surface pressure (the reduction in surface tension), relates surface tension and bulk concentration. The Frumkin equation (1.6) relates surface tension and surface excess concentration.

$$\gamma_0 - \gamma = \pi = -2.303 RT \Gamma_m \log \left( 1 - \frac{\Gamma_1}{\Gamma_m} \right)$$  \hspace{1cm} (1.6)

### 1.3 Micellization

Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but also because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles. The distortion of solvent structure can also be decreased (and the free energy of the solution reduced) by aggregation of the surface active molecules into clusters (micelles) with their correct orientation towards the solvent. The concentration at which this phenomenon occurs is called the critical micelle concentration (CMC). The determination of the CMC value for a particular surfactant can be made from, the breaks in the electrical conductivity/ surface tension/ light scattering, or fluorescence spectroscopy versus Surfactant concentration curves. Critical micelle concentrations have also very frequently been determined from the change in the spectral characteristics of some dyestuff added to the surfactant solution when the CMC of the latter is reached, this method is also called as Dye solvatochromism method.

Micelles of various shapes are possible. They normally acquire shapes of spherical, cylindrical, lamellar. The volume $V_H$ occupied by the hydrophobic groups in the micellar core, the length of the hydrophobic group in the core $l_c$, and the cross-sectional area $a_0$ occupied by the hydrophilic group at the micelle–solution interface are used to
calculate a “packing parameter,” \( V_H/lca_0 \), which determines the shape of the micelle.

\[
P = \frac{V_H}{lca_0}
\]  

(1.7)

\[
V_H = 27.4 + 26.9 \times n, \ l_c = 1.5 + 1.26n
\]

Where, \( P \) = Packing parameter, \( V_H = \) Volume of hydrophobic chain (\( \text{Å}^3 \)), \( l_c = \) length of the hydrophobic chain (\( \text{Å} \)), \( a_0 = \) Area of hydrophobic head group (\( \text{Å}^2 \)), \( n \) is the number of carbon atoms of the chain, or one less) and \( a_0 \) can be calculated as,

\[
a_0 = \frac{10^{20}}{N \Gamma}
\]  

(1.8)

Where, \( N \) is the Avogadro’s number, \( 6.023 \times 10^{23} \) and \( \Gamma \) is in \( \text{mol}/m^2 \)

The value of \( P \) gives fair idea about the structure of the micelle (1.1).

### Table 1.1: Packing Parameter values

<table>
<thead>
<tr>
<th>Values of ( P )</th>
<th>Structure of Micelle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 0.33</td>
<td>Spherical</td>
</tr>
<tr>
<td>0.33 - 0.5</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>0.5 - 1</td>
<td>Vesicles</td>
</tr>
<tr>
<td>&gt;1</td>
<td>Inverse micelles in non-polar media</td>
</tr>
</tbody>
</table>

### 1.3.1 Factors Affecting CMC

The factors known to affect the CMC in aqueous solution are:—

1. The structure of the surfactant,
2. The presence of added electrolyte in the solution,
3. The presence of various organic compounds,
4. The presence of a second liquid phase, and
5. The temperature of the solution.
1.3.2 Methods For The Determination of CMC

1.3.2.1 Equilibrium Surface Tension Measurement:

A typical experiment involves measuring the surface tension as a function of surfactant concentration. Prior to micelle formation an increase in the surfactant concentration, decreases the surface tension due to adsorption of the surfactant to the surface. Beyond the CMC, the surface is saturated with the adsorbed surfactant molecules ($\Gamma_{\text{max}}$ is reached) and any additional surfactant monomers added forms micelles (Figure 1.5). As a result the surface tension does not decrease further. The break in the surface tension isotherm is considered as the point at which micellization begins.

1.3.2.2 Conductivity Measurement:

This method is suitable for ionic surfactants in the absence of added electrolyte. In the premicellar region, equivalent conductivity of surfactant solution plotted against the square root of concentration decreases slightly but linearly. The surfactant behaves like a conventional electrolyte. However above the CMC, there is a large decrease in equivalent conductivity of the surfactant solution, due to incomplete dissociation of the surfactant in micellar form. The micelles are less efficient carriers of charge than the equivalent number of fully dissociated monomers. The surfactant concentration at which the equivalent conductivity begins to fall rapidly is taken as the CMC of the surfactant.

1.3.2.3 Dye Solvatochromism:

This method involves the use of solvatochromic dye molecule. These molecules absorb radiation at different wavelengths in different environments. The dye molecule is chosen such that it absorbs at a different wavelength in the hydrophobic core of the micelle (nonpolar) than in the aqueous environment (polar environment). Thus the surfactant concentration around which a change in the wavelength of absorption (of the dye molecule) occurs, is considered as the onset of micellization.
1.3.2.4 Reduction of Surface Tension

A surfactant molecule has a tendency to adsorb at the interface and thereby decreasing the free energy of the interface. The molecules at the surface of a liquid have potential energies greater than those of similar molecules in the interior of the liquid. An amount of work equal to this difference in potential energy must be expended to bring a molecule from the interior to the surface. The surface free energy per unit area, or surface tension, is a measure of this work; it is the minimum amount of work required to bring sufficient molecules to the surface from the interior to expand it by unit area. The amount of surfactant present at the interface, i.e. surface excess concentration of the surfactant, can be estimated by the Szyskowski equation (1.5).

1.3.2.5 Efficiency and Effectiveness of a surfactant

The efficiency of a surfactant in reducing surface tension can be measured by the same quantity that is used to measure the efficiency of adsorption at the liquid–gas interface $p_{C_20}$, the negative log of the bulk phase concentration necessary to reduce the surface tension by 20 dyn/cm (mN/m). The effectiveness of a surfactant in reducing surface tension can be measured by the amount of reduction, or surface pressure, $(\pi_{CMC} = \gamma_0 - \gamma_{CMC})$ attained at the critical micelle concentration, since reduction of the surface tension beyond the CMC is relatively insignificant (Figure 1.5).
Figure 1.5: Surface tension versus surfactant concentration plot