CHAPTER 1

Introduction

1.1 SURFACTANTS

The surface-active agents have been utilized by nature and human beings for many centuries. For instance, from the excavation of ancient Babylon, soap-like material was obtained from clay cylinders. It revealed that the method of making soap was known even in 2800 BC. According to the inscriptions present on these cylinders, it was prepared by boiling fats with ashes but was not named as ‘soap’. The Phoenicians show history of soap around 600 BC. Pliny the Elder recorded in *Historia Naturalis* (around AD 70) the manufacture of soap using fat and wood ashes [1]. On the industrial scale, the manufacturing of soap was started in the middle of 19th century. However, the utilization of natural sulphonated oils was initiated for making soap during the last part of the 19th century whereas the synthetic surfactants were prepared and consumed on a large industrial scale in 1950s.

There are many reasons for the current interest in the field of surfactant chemistry. Firstly, due to the decreasing resources of crude oil, surfactants are being used in the enhanced oil recovery processes for extracting petroleum products. Secondly, due to the biological effects of the synthetic surfactants on mankind, far more intense investigations are being carried out in the field of ‘Green Chemistry’. Moreover, the substantial growth in the field of biochemistry has disclosed that many biological processes rely upon the surface activity, for instance, the penetration of cell walls by invading viruses. Nature also depends heavily on surfactant chemistry, for instance, lungs use the surfactants to maximize the efficiency of gas exchange.

The term surfactant is a combination of the phrase ‘surface active agent’ and is defined as any substance which strongly adsorbs at a surface or interface. Surfactants have amphiphatic molecular structure consisting of a nonpolar hydrocarbon portion and a polar ionic portion. The hydrocarbon portion interacts very weakly with water molecules in aqueous environment and is usually called hydrophobic tail. The polar or ionic portion of the molecule interacts strongly with water molecules via dipole-dipole or ionic–dipole interactions and is solvated. This polar portion is called the hydrophilic head or the ionic head group. Under appropriate conditions of temperature and concentration, some surfactants have the ability to self assemble and form micelles in solution. This unique feature of surfactant molecules form the
basis for many practical applications in oil recovery, pharmaceuticals, formation of vesicle, synthesis of nanomaterials, emulsification, drug delivery, etc. [2–7].

The classification of surfactants depends upon the charge on their head groups. Surfactants, having a charged head group are known as ‘ionic’ surfactants whereas those with uncharged head groups are called as ‘nonionic’ surfactants. The ionic surfactants are further divided into anionic (negatively charged), cationic (positively charged) and zwitterionic (two charge groups of different sign) as shown in the Table 1.1.

Table 1.1: Classification of surfactants.

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>Sodium stearate</td>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{16}\text{COO}^- \text{Na}^+)</td>
</tr>
<tr>
<td></td>
<td>Sodium dodecyl sulfate</td>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{11}\text{SO}_4^- \text{Na}^+)</td>
</tr>
<tr>
<td></td>
<td>Sodium dodecylbenzene sulfonate</td>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{11}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+)</td>
</tr>
<tr>
<td>Cationic</td>
<td>Laurylamine hydrochloride</td>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{11}\text{NH}_3^+ \text{Cl}^-)</td>
</tr>
<tr>
<td></td>
<td>Dodecytrimethylammonium chloride</td>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{N}^+\text{(CH}_3\text{)}_3\text{Cl}^-)</td>
</tr>
<tr>
<td></td>
<td>Cetyltrimethylammonium bromide</td>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{15}\text{N}^+\text{(CH}_3\text{)}_3\text{Br}^-)</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Polyoxyethylene alcohol</td>
<td>(\text{C}<em>n\text{H}</em>{2n+1}(\text{OCH}_2\text{CH}_2)_n\text{OH})</td>
</tr>
<tr>
<td></td>
<td>Alkylphenol ethoxylate</td>
<td>(\text{C}<em>9\text{H}</em>{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH})</td>
</tr>
<tr>
<td>Zwitterionic</td>
<td>Dodecyl betaine</td>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{N}^+(\text{CH}_3\text{)}_2\text{CH}_2\text{COO}^-)</td>
</tr>
<tr>
<td></td>
<td>Lauramidopropyl betaine</td>
<td>(\text{C}<em>{11}\text{H}</em>{23}\text{CONH(\text{CH}_2\text{)}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-})</td>
</tr>
<tr>
<td></td>
<td>Cocamido-2-hydroxypropyl sulfobetaine</td>
<td>(\text{C}<em>n\text{H}</em>{2n+1}\text{CONH(\text{CH}_2\text{)}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH(OH)}})</td>
</tr>
</tbody>
</table>

1.2 MICELLE FORMATION AND CRITICAL MICELLE CONCENTRATION

At low concentrations, a surfactant molecule behaves like a normal electrolyte in aqueous solutions, but at higher concentration very different behavior results. It is due to the self assembling of large number of surfactant monomers into organized aggregates called as ‘micelles’, where the hydrophobic tail of the surfactant molecule resides in the interior of the aggregate and the hydrophilic head faces the aqueous medium (Fig. 1.1). The process of micelle formation or micellization in aqueous solutions can be considered as a compromise between the tendency of the polar part to keep contact with aqueous medium and the desire of the hydrocarbon tail to avoid energetically unfavorable contact with aqueous medium.
Fig. 1.1: Schematic diagram of micelle formation from surfactant monomers.

The overall changes in the Gibbs free energy of the system are determined by the relative contribution of electrostatic and hydrophobic interactions occurring during the micelle formation [8]. The limited solubility of the hydrophobic part of the surfactant molecule in aqueous solutions has been attributed to the ‘hydrophobic effect’. The transfer Gibbs free energy is defined as the ‘Gibbs energy for the process of transferring the hydrocarbon solute from the hydrocarbon solvent to water’. The enthalpic and entropic contributions towards the Gibbs free energy transfer show that the entropy term is dominant factor for the ‘hydrophobic effect’ or in other words the ‘transfer of the hydrocarbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy’ [9]. The breaking of the hydrogen-bonded structure of water and subsequent formation of some other water structures known as ‘icebergs’ around the hydrophobic tails result in the decrease in entropy. However, due to the availability of hydrophobic component, the water molecules present in the neighborhood tend to get ordered. In an attempt to limit the involvement of large number of water molecules and to decrease the large entropy changes, the ‘icebergs’ form clusters [10]. This process is favored enthalpically but is unfavorable entropically. The net result of the process is to bring the hydrophobic tails closer to each other and this is known as ‘hydrophobic interactions’. On the other hand, water molecules try to return to their original tetrahedral structure and this effect is known as ‘molecular interactions’. The attractive forces between the hydrophobic tails result in their removal from the water ‘iceberg’, leading to aggregation of the molecules.

The adsorption of surfactant molecules takes place at air/water interfaces even at very low surfactant concentrations due to the ‘hydrophobic effect’. The air/water interface takes some time to acquire equilibrium due to continuous adsorption/desorption from the interface. Hence, the interface is always in a state of dynamic equilibrium as a consequence of surfactant activity. This surfactant activity can be evaluated by the measurement of surface or
interfacial tension at varying concentrations and time. At certain specific concentration of the surfactant, called as the critical micelle concentration (CMC), the molecules of the surfactant assemble to form ‘micelles’. The CMC value of a surfactant is its characteristic property which further depends upon a number of factors such as the presence and nature of the solvent, pressure, pH, temperature, etc. The micelle formation also depends upon the balance of electrostatic, hydrophobic and thermal forces. The CMC values of a surfactant can be lowered by (i) the addition of the salt (ii) decreasing temperature and (iii) increasing the chain length of the hydrophobic part of the molecule. The transfer of surfactant monomers from aqueous solutions to micelles takes place in a range of concentrations. The surfactants form spherical micelles consisting of 50-100 monomer units at concentration slightly above the CMC. The features of the micellar core, consisting of hydrophobic chains, are almost similar to that of the liquid hydrocarbon. For an anionic surfactant such as sodium dodecyl sulphate,

![Diagram](image.png)

**Fig. 1.2: Variation of physicochemical properties of surfactant solutions above and below the CMC value** (Source: A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, John Wiley Sons, Inc. NY, pp. 480, 1997).
the variations of the physicochemical properties around CMC value are shown in Fig. 1.2 using different techniques. It can be seen that below the CMC value, the surfactant behaves like a strong electrolyte. However, above the CMC value, the properties change significantly due to self assembling nature of the surfactant.

The knowledge of the CMC value of a surfactant is very important in order to establish its suitability for different applications. The process of micelle formation can be described using different models. Among these models, the pseudo-phase separation model treats micelles as a separate phase and defines CMC as the ‘concentration of maximum solubility of the monomer in that particular solvent’. However, this model has some drawbacks but the depiction of CMC is very helpful for obtaining different thermodynamic parameters and properties [8]. Therefore, this model is most frequently utilized for the calculation and discussion of various thermodynamic properties.

The CMC values are important in virtually all industrial applications, such as drug encapsulation, surface properties, cosmetics, food processing, disinfectants, etc. [11–13]. Moreover, in certain applications such as formations of emulsions, stabilization of suspensions and foams, lowering of surface and interfacial tension or processing of minerals, the maximum influence of the surfactants is attained when sufficient numbers of micelles are present in the solution [14]. It is possible only if the concentration of surfactants present in the aqueous solutions is much higher than their CMC values. Above the CMC value, the increase in the adsorption of the surfactants at the air/solution interface is very little. Therefore, CMC value also denotes the concentration of the surfactant at which the maximum possible adsorption of the surfactant takes place.

1.3 FACTORS AFFECTING THE CMC IN AQUEOUS SOLUTIONS

The properties of surfactant solutions change when the micelle formation begins and a large number of studies have been carried out by paying attention on the determination of the CMC values under different conditions. Many investigations have also been reported on elucidating the factors responsible for the micelle formation in aqueous and non aqueous solutions [15]. The factors affecting the micelle formation in aqueous media have been described below.

1.3.1 The Structure of the Surfactant

The CMC of surfactant depends upon the length of the hydrophobic tail, hydrophilic head group and degree of dissociation of the counterions.
(a) The Hydrophobic Group: The CMC of a surfactant decreases as the hydrophobic chain length of the surfactant molecule increases in aqueous solutions. In case of nonionic and zwitterionic surfactants, the decrease is comparatively more as the hydrophobic chain length is increased, for instance, there is a reduction in CMC values by nearly $\frac{1}{10}$ with the addition of 2 methylene groups in the hydrophobic chain. Similarly the decrease due to the presence of a phenyl group attached to the hydrophobic chain is almost equal to $3\cdot\frac{1}{2}$ methylene groups. However, when the hydrophobic chain contains greater than 16 carbon atoms, then the fall in CMC values do not follow this trend. Further, when the number of carbon atoms in the hydrophobic chain is greater than 18, the CMC values vary insignificantly with subsequent addition of methyl groups because of intermingling of the chains.

The carbon atoms on the branched hydrophobic group decrease the CMC values to a lesser extent than those in straight hydrophobic chains. The presence of double bonds instead of single bonds in the hydrophobic chain results in the increase in CMC values. Similarly, the trans form of a compound has lower CMC than that of cis form due to steric hindrance. The presence of bulkiness either in hydrophobic chain or in hydrophilic head group of the surfactant appears to exhibit higher CMC in comparison to those having same number of carbon atoms in the linear chain. It is because the inclusion of bulky hydrophobic group inside the micellar core becomes difficult which result in the increase in CMC [16]. The polarity of a functional group within the hydrophobic chain also leads to the increase in CMC of the surfactant in aqueous solutions [17]. In case of a nonionic surfactant containing both ethylene oxide (EO) and propylene oxide (PO) groups, the CMC of the surfactant increases with the increase in EO groups although a decrease in CMC is observed with the increase in PO groups [15].

(b) The Hydrophilic Group: The CMC of ionic surfactants is much higher than those of nonionic surfactants in aqueous solutions for same length of hydrophobic tail whereas zwitterionic surfactants have a little lower CMC as compared to ionic surfactants. An increase in the CMC results when the hydrophilic group is present in the middle of the hydrophobic chain instead of either side of the chain. It is due to the fact that the length of the hydrophobic group decreases on either side of the hydrophilic head leading to decrease in the hydrophobic interactions. Further, it has been reported that if the ionic hydrophilic group is nearer to the terminal carbon, then CMC will be more [15]. It is because of the increase in the electrostatic potential of the surfactant ion when the ionic group of a surfactant is shifted
from the aqueous solution to the neighborhood of the hydrophobic micellar core due to micelle formation. A comparison among the quaternary cationic surfactants suggests that the surfactants possessing trimethylammonium head group show higher CMC than those containing pyridinium head groups. It is because of greater difficulty in packing of the tetrahedral structure of trimethylammonium head groups into the micellar core as compared to planar pyridinium head groups of the surfactant molecule.

![Figure 1.3](image)

**Fig. 1.3: Variation of slopes before ($S_1$) and after ($S_2$) the CMC in specific conductivity versus surfactant concentration plot.**

c) Degree of counterion binding to the Micelle: In aqueous solutions the break in the specific conductance ($\kappa$) versus concentration of an ionic surfactant indicates the CMC as shown in Fig. 1.3. The binding of the counterions to the micellar surface of the surfactant causes the break in the plot. The ratio of the slopes above ($S_2$) and below ($S_1$) the CMC point, represent the degree of dissociation ($g$) of the counterions [9]. The term $(1 - g)$ denotes the degree of binding ($h$) of the counterion to the micelle of a surfactant. The values of $g$ are affected by the changes in the solvent properties which in turn affect the CMC of the surfactant. For instance, in aqueous solutions, a decrease in CMC is due to increase in binding of the counterions of the surfactant. Similarly, the binding of the counterion increases with polarizability and the charge of the counterion. However, as the hydrated radius of the counterion increases, its binding decreases [15].
1.3.2 Presence of Electrolyte and Solvent

The presence of electrolyte and solvent in aqueous solutions of surfactants results in a change in the CMC. This phenomenon is more significant in ionic than in zwitterionic surfactants which in turn is more significant than in nonionics. In presence of an electrolyte in aqueous solutions, the CMC of the surfactants change. It is caused by the phenomena of ‘salting out’ or ‘salting in’ of the hydrophobic chains [18]. The increase in degree of hydrophobic interactions (depending upon the type of electrolyte) may be due to decrease in the solubility or ‘salting out’ of the hydrophobic chains present in the aqueous electrolytic solutions. The capability of an electrolyte to ‘salt out’ a certain type of solute depends upon its ionic strength. However, with the increase in charge density of an ion, the phenomenon of ‘salting out’ also increases. These results are more applicable in case of anions as compared to cations and become important at intermediate electrolytic concentrations (0.1 – 1 M). An ‘increase in the solubility or salting in’ of the hydrophobic chains present in the aqueous electrolytic solutions is observed only for very large ions and in case of very small non polar solutes. Moreover, the property of an ion to ‘salt out’ or ‘salt in’ is determined whether the ion is ‘water structure maker’ or ‘water structure breaker’. The ‘water structure maker’ ions are highly hydrated and have high charge density/radius ratio, e.g., F\(^-\) ions. These ions decrease the CMC by ‘salting out’ the hydrophobic chains of the surfactant monomer. On the other hand, the ‘water structure breaker’ ions are weakly hydrated with low charge density/radius ratio, e.g., CNS\(^-\) ions. Such ions increase the CMC by ‘salting in’ the hydrophobic chains of the surfactant monomer.

Micelle formation in mixed solvent solutions has not received much consideration in comparison to the detailed and widespread studies on surfactant solutions in aqueous medium [9]. The phrase ‘solvophobic interaction’ is applicable for denoting the micelle formation in mixed solvent solutions as compared to ‘hydrophobic interaction’, which is used to describe the micelle formation in aqueous solutions. Moreover, the process of micellization is not dependent upon the exclusive property of the water to form network structure as a result of hydrogen bonding [19]. For a surfactant, the micellization in aqueous mixed solvent solutions is not as favorable as in aqueous solutions (Fig. 1.4) but is analogous in many ways to those in aqueous solutions [20]. Among various solvents, alcohols are most commonly studied solvents as they are of utmost significance in a number of industrial applications such as formulations, cosmetics, dyes, etc. [21–22]. These applications are based upon the influence of alcohols on the CMC and other thermodynamic properties [23–24].
micellar structure strongly depends on the amount of alcohol added. In addition, the micellar size varies with the hydrophobic/hydrophilic properties of the alcohol. For instance, the longer chain alcohols participate in the micelle formation and may even turn out to be an essential part of the micellar core [25].

1.3.3 Temperature of the Solution

The variation of CMC with temperature in aqueous solutions depends upon the range of temperature being investigated [15]. The CMC values for ionic surfactants initially decrease with increase in temperature to a lower value and then increase with subsequent rise in temperature. The CMC dependence on temperature of nonionic and zwitterionic surfactants is not as predictable although it has been found that some nonionic surfactants reach the CMC minimum at around 50 °C. The increase in the temperature results in decrease in hydration of the hydrophobic groups, a factor which favors micelle formation [9]. However, the increase in temperature also leads to in the disruption of the structure of water surrounding the hydrophobic groups, a factor that opposes micelle formation. Therefore, these two factors determine the increase or decrease in the CMC values over the temperature range studied.
1.4 MODELS OF MICELLE FORMATION

Generally two types of models are being used in describing the micelle formation process. They are the pseudo-phase separation model [26–28], which treats micelles as separate phase formed at and above the CMC, and the mass-action model [29–30], which considers surfactant monomer in solution to be in equilibrium with surfactant micelles. An extension of mass action model is the multiple equilibria model [31], which considers the formation of aggregates of various sizes, accounting for the observed polydispersity in aggregation numbers. However, this introduces a large number of variables into any analysis of experimental data making it difficult to apply. The pseudo-phase model has been shown to account for, at least semi-quantitatively, the observed concentration dependence of apparent molar properties and in deriving thermodynamic functions of micellization. The main criticism of this model is that calculated values often show substantial deviation from experimental values for some properties, particularly if the transition from monomer to micelle formation takes place over a larger concentration range.

Nevertheless, due to simplicity of its application, the pseudo-phase model is widely used to model thermodynamic data, particularly for long chain surfactants having low CMC values. The mass action model allows for modeling of thermodynamic properties over a broader concentration range in the pre-micellar range as opposed to the pseudo-phase model which is applicable only in the post-micellar range.

1.4.1 Pseudo-Phase Separation Model

As stated above, the pseudo-phase separation model considers the formation of micelles to constitute the formation of a separate phase [26]. The chemical potential of the non-ionized monomeric surfactant $\mu_S$ is given by

$$\mu_S = \mu_S^o + RT \ln a_S \quad \ldots \quad (1.1)$$

where $\mu_S^o$ is the standard state chemical potential of the monomer surfactant and $a_S$ is the activity of the surfactant monomer. It is assumed that that the concentration of free monomers is low and thus activity $a_S$ of the surfactant monomer can be replaced by its mole fraction $X_S$. Therefore, the above Eqn. (1.1) can be written as

$$\mu_S = \mu_S^o + RT \ln X_S \quad \ldots \quad (1.2)$$
If $\mu_M$ denote the chemical potential of the surfactant in the micellar form,

$$\mu_M = \mu_M^o + RT \ln X_M \quad \ldots \quad (1.3)$$

where $\mu_M^o$ denotes the chemical potential in the standard state and $X_M$ is the mole fraction of the micelles in the micellar form.

Since $X_M = 1$, therefore $\mu_M = \mu_M^o \quad \ldots \quad (1.4)$

The standard Gibbs free energy change for transfer of one mole of surfactant form solution to micellar phase, ($\Delta G^o_{\text{mic}}$), is given by

$$\Delta G^o_{\text{mic}} = \mu_M^o - \mu_S^o = \mu_M - \mu_S + RT \ln X_S \quad \ldots \quad (1.5)$$

At equilibrium, the chemical potential of the surfactant in the monomer and micellar form ($\mu_S$ and $\mu_M$ respectively) are equivalent thus

$$\mu_S = \mu_M$$

Therefore, from Eqn. (1.5),

$$\Delta G^o_{\text{mic}} = RT \ln X_S \quad \ldots \quad (1.6)$$

If CMC can be considered to be the solubility limit of the free monomer, then $X_S = X_{\text{CMC}}$ and therefore, Eqn. (1.6) becomes

$$\Delta G^o_{\text{mic}} = RT \ln X_{\text{CMC}} \quad \ldots \quad (1.7)$$

If $n_s$ and $n_{\text{H}_2\text{O}}$ denote the number of moles of surfactant and that of water in solution respectively,

Since $n_s$ is much less than $n_{\text{H}_2\text{O}}$ therefore,

$$X_{\text{CMC}} = \frac{n_s}{n_s + n_{\text{H}_2\text{O}}} \approx \frac{n_s}{n_{\text{H}_2\text{O}}}$$

Converting into concentration units, the Eqn. (1.7) becomes,

$$\Delta G^o_{\text{mic}} = RT \left[\ln \text{CMC} - \ln 55.5\right]$$
where 55.5 is the molar concentration of water at 298.15 K. The above treatment does not consider the case of ionic surfactants, for which one must take into consideration the transfer of a portion of counterions into the micellar phase. If \( h \) is the number of moles of counterions associated per mole of monomers in the micellar phase and is known as degree of counterion binding. If one mole of micelle consist of \( n \) moles of surfactant monomers and \( m \) moles of counterions, then \( h = \frac{m}{n} \). Further, it is also considered that the free counterions present in solution phase are in equilibrium with the counterions bound to the micelle. Hence, for ionic surfactants Eqn. (1.7) modifies to

\[
\Delta G^0_{\text{mic}} = RT \ln X_{\text{CMC}} + h RT \ln X_{C} \quad \ldots\ldots (1.8)
\]

where \( X_{C} \) is the mole fraction of counterions in the solution. At CMC, where the micellar phase is just formed, it can be approximated that \( X_{C} = X_{\text{CMC}} \). Therefore, Eqn. (1.8) becomes

\[
\Delta G^0_{\text{mic}} = (1 + h) RT \ln X_{\text{CMC}} \quad \ldots\ldots (1.9)
\]

If \( g \) denotes the degree of counterion dissociation, then \( g = 1 - h \)

\[
\Delta G^0_{\text{mic}} = (2 - g) RT \ln X_{\text{CMC}}
\]

\[
= (2 - g) RT [\ln \text{CMC} - \ln 55.5]
\]

For ionic gemini surfactants, which dissociate into three ionic species, the term \( 2 - g \) is replaced by \( 3 - 2g \) [9].

1.4.2 Mass Action Model

The mass action model is more appropriate description of the micellar process as it considers the surfactant monomer and micelles to be in equilibrium with one another [29–30], i.e.,

\[
K_M
\]

\[
\frac{nS}{M}
\]

where \( M \) refers to a micelle comprised of \( n \) monomers of surfactant \( S \). The equilibrium constant for the micelle formation process, \( K_M \), is given by

\[
K_M = X_M / X_S^n \quad \ldots\ldots (1.10)
\]

where \( X_M \) and \( X_S \) are the mole fractions of micelles and monomers, respectively. The molar Gibbs energy due to micelle formation is calculated using Eqn. (1.10) as:
\[ \Delta G_{\text{mic}}^\circ = -\frac{RT}{n} \ln K_M = \frac{RT}{n} \left[ n \ln X_S - \ln X_M \right] \]

To obtain an expression for \( \Delta G_{\text{mic}}^\circ \) as a function of the CMC, one must then relate \( K_M \) to the CMC. A number of methods have been employed to do this, all of which are dependent upon the definition of the CMC used. For example, Moroi [32] has derived an expression for \( K_M \) as a function of the CMC based upon strict definition of the CMC given by Philips [33], while Desnoyers et al. [31] have derived an expression based upon the concentration at which the fraction of surfactant in the monomer form shows an inflection. Regardless of which definition is used for the CMC, the resulting expression for \( \Delta G_{\text{mic}}^\circ \) is usually a function of both the CMC and the aggregation number for the micelles formed.

### 1.5 GEMINI SURFACTANTS

In the past few decades the studies involving gemini surfactants have become an important field of focus in colloidal research [34]. These surfactants are so named due to their interesting structure, which can be represented as two monomeric surfactants connected by the head groups through a spacer [35–36] as shown in Fig. 1.5. The word ‘gemini’ was originally assigned to bis-surfactants having rigid spacers (such as a benzene or stilbene system) in 1991 [37]. Since then the term ‘gemini’ is being utilized for all the double chain surfactants irrespective of the nature of the spacer group. Among different types of the gemini surfactants, the most commonly used gemini surfactants are the 1, 2 - ethanediyl bis(dimethylalkylammonium bromide) surfactants, known as ‘m-s-m’ gemini surfactants, where ‘m’ is the number of carbon atoms attached to the alkyl tails of the surfactant and ‘s’ is the number of carbon atoms belonging to the unsubstituted alkyl spacer group.

![Fig. 1.5: Schematic diagram showing the structure of a gemini surfactant.](image-url)
The CMCs obtained for the gemini surfactants are lower as compared to those of conventional single chain surfactants (monomeric surfactants) by typically an order of magnitude or more. This decrease is among the primary rationale for the focus on the gemini surfactants and can be explained simply by considering that the two alkyl chains (as compared to one in conventional surfactants) are shifted simultaneously from the aqueous to the micellar phase. The CMC values of the gemini surfactants decrease with the increase in total number of carbon atoms in the surfactant molecule as in case of conventional surfactants. However, when the number of carbon atoms per alkyl chain of the gemini exceeds 14 the linear relationship is not followed due to coiling of these long chains [37].

The adsorption of gemini surfactants at the air/water interface lead to the distortion of the water structure by hydrophobic groups [38]. Since a single molecule contains two hydrophobic groups, it should be quite disruptive, therefore, promoting migration of micelles to the air/water interface (Fig. 1.6). Menger and Keiper [39] believe that any selective changes in water structure are likely due to interfacial packing effects. They interpret the small cross-sectional areas of gemini surfactant, at a saturated air/water interface, to tight packing at the interface, which in turn provides an efficient lowering of the surface tension.

![Fig. 1.6: Position of gemini surfactant monomer at (a) interface and in (b) micellar phase](Source: J. Zhao, Y. Deng, X. Pei, Colloids Surf. A 364 (2010) 87–93).

The flexibility of chain length and hydrophobicity of the spacer between two hydrophilic head groups also influence the CMC and adsorption at the air/water interface. An important and useful characteristic of gemini surfactants is their stuffing efficiency at different interfaces. Smaller the linkage between the two hydrophilic groups, closer will be the stuffing of the two hydrophobic groups of the gemini than those of conventional surfactants at the air/solution interface. On certain occasions, even the formation of multilayers may take place.
Thus, a substantially thick coherent film of the gemini surfactants is formed at the interface and is apparent in their enhanced emulsifying and foaming properties. It also accounts for unusually high viscosity shown by some gemini surfactants.

1.6 POLYMERS

Polymers are macromolecules which are produced by combining smaller units known as monomers. The repeating groups are linked together through covalent bonding. Naturally occurring polymers include polysaccharides such as cellulose, proteins and enzymes. There are also a large number of synthetic polymers such as nylon, polystyrene, polyethylene oxide, polyacrylamide which have widespread use in industry [40]. Since the beginning of civilization, the polymeric materials, possessing high molecular weights, are being used to provide colloidal stability. For instance, the polymeric materials occurring in nature such as animal glues, gum arabic and egg white are being utilized for the preparation of metal oxide pigments, paints, water based inks and varnishes. Gum arabic (Acacia gums) mainly contains carbohydrate but also includes 2 – 3% protein which is a significant ingredient of its

![Diagram of Polysaccharide and Polypeptide](image)

Fig. 1.7: Maturation of gum arabic resulting in the agglomeration of the protein containing subparts of the substance and forming a network of cross-linked hydrogel. (Source: S.K.H. Gulrez, S. Al-Assaf, G.O. Phillips, Hydrogels: Methods of Preparation, Characterization and Applications. In: A. Carpi (ed.) Progress in Molecular and Environmental Bioengineering - From Analysis and Modeling to Technology Applications, Chap. 5, Janeza Trdine 9, 51000 Rijeka, Croatia, 2011).
structural feature [41]. The protein part of gum arabic has been subdivided into three categories depending upon the molecular weight. These are (i) glycoprotein (GP) (ii) arabinogalactan (AG) and (iii) arabinogalactan protein (AGP) as shown in Fig. 1.7.

After the heat treatment, the molecular weight of the constituents containing protein, increases and consequently a hydrogel is obtained having superior mechanical characteristics and water retaining capability [42]. By controlling the maturation process, the molecular changes occurring during the preparation of gum arabic, can be evaluated. Thus, the hydrogels with desired molecular dimensions having accurate structure can be produced and a substantial quantity of high molecular weight protein constituent (AGP) can be obtained by maturation of the gum due to transfer of the proteins having low molecular weight constituents. This phenomenon was named as ‘protection’ in the beginning of the 20th century. It meant that an adsorbed layer of the polymer material protects the dispersion from flocculation and coagulation. In aqueous phase dispersions of inorganic materials, the most common source of colloidal stability was ‘electrostatic stabilization’ where ionic surfactant or polyelectrolyte was used to stabilize the agglomerate (Fig. 1.8).

In non-aqueous media, the stabilization of the dispersion depends upon the solvent characteristic and their influence on various forces responsible for attaining the stability. The effect of van der Waal forces of attraction between the particles and the low dielectric constant of the medium results in the compression of the electric double layer. Therefore, the only way to achieve colloidal stability in these situations is the ‘protection’ offered by the adsorbed layer of the surfactant or the polymeric substance. In the past, glycerides of fatty acids based upon the natural oils and long chain alkyl resins or synthetic resins based upon the natural fatty acids, were utilized for this purpose. But, with the advancement of technology, more efficient and useful surfactants and polymeric materials are being employed for manufacturing, painting and coating materials. Moreover, due to the requirements of new and improved materials for modern applications (such as nanotechnology, biotechnology and electronic materials), light weight and composite materials are required. Hence, the utilization of polymers has increased significantly and therefore, the studies involving these advanced materials have gained momentum in recent times.

In an ideal aqueous polymer solution, the interactions between water and polymeric molecule are more favorable enthalpically than among the polymer molecules themselves. Thus the interactions between polymer chains are negligible in aqueous solutions. The thermodynamic behavior of aqueous polymer solution is opposed when the polymer molecules tend to associate. At higher concentrations, these effects tend to reach equilibrium at some situation of solvency and temperature. At these temperatures and concentrations of the polymer, the solution tends to behave ideally. Such situations were explained by Flory [43] and are commonly called as ‘theta conditions’. The size of the molecular coil of a particular polymer is dependent on the type of the solvent used. A good solvent expands the coil whereas on the other hand a poor solvent causes shrinkage. In between the two, the theta solvents are found,

![Fig. 1.9: Random coils in solvents of different solvent power; $\alpha$ is the linear coil expansion factor which is equal to one in a theta solvent](Source: www.atarnotes.com).
for which, the measured characteristics of the polymer are not dependent on the solvent properties (Fig. 1.9). These characteristics depend upon the properties of the polymers i.e., sterically favored rotations, bond length and bond angle. Under these conditions, the aqueous polymer solution exhibit similar behavior as expected from the ‘ideal chain model’. In addition, the bulk phase of the polymer also justifies the ‘theta conditions’ according to which, the bulk polymer phase attains similar confirmations as were attained by the polymer dissolved in theta solvents.

Under theta solvency condition or at theta temperature, for a given polymeric solution, it has been observed that the colloidal dispersion which has been stabilized by the high molecular weight polymer, will on many occasions, tend to flocculate. These conditions have been experimentally analyzed by Napper [44] and the results reveal that a colloidal dispersion will be stabilized by the polymer if the solvent utilized for the purpose is ‘better than theta’ solvent. An important conclusion drawn on the basis of these observations indicate that only few solvents can be utilized for the preparation of polymeric materials that stabilizes a colloidal dispersion. Therefore, development of polymeric material for all types of applications is not possible.

1.7 TRIBLOCK POLYMERS

The triblock polymers (TBPs) are classified as nonionic surfactants and commonly called as ‘Block Copolymers’. These TBPs are available in the market as Pluronics® and contain a hydrophobic polypropylene oxide block OH[-CH(CH₃)-CH₂-O] denoted as (PPO) connected with two hydrophilic polyethylene oxide blocks OH[-CH₂-CH₂-O] denoted as (PEO) on either side which is represented as PEO-PPO-PEO (Fig. 1.10). The ratio of molecular weights of PEO and PPO determines the hydrophilic-lipophilic balance (HLB) and these HLB values further evaluate their polymorphic character [45]. The TBPs possessing different molecular weights and PPO/PEO ratios are available in the market. The solubility of these TBPs in aqueous phase increases with the number of PEO blocks. These polymers are used in a large number of pharmaceutical applications such as formulations and emulsifications [46]. The essential industrial uses of these TBPs include drug transport, synthesis of nano materials, extraction, processing of waste materials, etc. [47–54]. Hence, the studies on solution properties of these materials have vast significance.

Since, these polymers contain both hydrophobic and hydrophilic part in the same molecule, therefore, they exhibit several additional benefits in comparison to the nonionic polymers.
Further, the block copolymers have certain similarities with the amphiphiles such as formation of aggregates of varying shapes which further depend upon the number of PPO and PEO blocks, type of the solvent and the temperature of the solution. These polymers are available as paste or solid depending upon their molecular mass [55]. The mechanism of growth for different blocks can be modulated which controls the phase transition. This provides a new method for controlling the morphology that is appropriate in certain specific conditions [56–57].

The nonionic character of the TBPs limits the method required to study their aggregation behavior as compared to those for charged amphiphiles. The aggregation or micellization of these polymers is more complex than for charged counterparts and is influenced remarkably by their hydrophobicity [58–61]. Further, the blocks in a TBP are not distributed uniformly for copolymers possessing almost same molecular weights. Hence, distinct values of CMC and critical micelle temperature (CMT) can not be evaluated in case of these polymers. Thus, the CMC values of TBPs have a range of concentrations in comparison to those for ionic surfactants. However, the CMC values of the TBPs are strongly dependent upon the temperature which results in the variation of physicochemical properties of their aqueous solutions [61]. The aggregation behavior of such systems have been studied using different methods including surface and interfacial tension, viscosity, density, neutron and light scattering, etc. [62].

![Schematic representation of general structure of a triblock polymer and micelle formation.](Fig. 1.10: Schematic representation of general structure of a triblock polymer and micelle formation. (Source: V. Singh, P. Khullar, P.N. Dave, N. Kaur, Int. J. Ind. Chem. 4:12 (2013) 1–18).)
As the amount of TBP in aqueous solution is increased, the aggregation begins near the CMC and at a temperature close to CMT. The temperature dependence of micelle formation in TBPs can be understood as follows. With the increase in temperature of the solution, the hydrophobic PPO blocks start losing the hydration sphere, causing enhanced hydrophobic interactions among these blocks. However, the PEO blocks maintain their strong interactions with water molecules. Hence, the different behavior of the two parts of the same molecule induces the micelle formation as in conventional amphiphilic molecule. The spectroscopic studies indicate [63] that the micelle consist of a hydrophobic ‘core’ constituted by weakly hydrated PPO blocks. The fully hydrated PEO blocks are situated in an outer shell called ‘corona’ and surround the core (Fig. 1.10). However, the less hydrophobic TBP, due to large number of PEO blocks, do not aggregate at low temperatures. But these polymers start aggregating as the temperature is increased because water becomes a poorer solvent for both ethylene oxide and propylene oxide groups at these temperatures. Moreover, the relative influence of PPO-PPO, PEO-PPO and PEO-PEO interactions are also temperature dependent [46]. It seems that the stronger PPO-PPO attractions overcome the PEO-PEO repulsions at higher temperatures which results in the micelle formation at lower concentrations. Hence, micelle formation is mainly a function of number of PPO blocks and the temperature. However, the influence of temperature on micellar and mixed micellar properties of TBPs have been investigated rarely [59–60]. The effect of temperature on the hydration of the PEO and PPO blocks of TBPs influences the hydrophobicity of TBP micelles and its stability. Therefore, the mixed micellar study of these TBPs with conventional and gemini surfactants is of fundamental and industrial significance.

1.8 SURFACTANT-POLYMER INTERACTIONS

The widespread applications of surfactant-polymer systems in industry have generally been a result of the observed enhancement of solution properties brought about by the combination of the surfactants and polymers. These applications [64] can be found in nearly any aspect of daily life ranging from the industrial products (such as lubricants, paints, detergents, cosmetics, adhesives and coatings) to biological systems (e.g. the structure and functioning of membranes, and lipid transport). In such systems the surfactant provides control over interfacial tension, emulsification capacity and colloidal stability, while the polymer provides control of the rheological properties as well as colloidal stability [65]. In addition, the combination may also increase the solubility of one or the other component e.g. the increase in cloud point of surfactants in the presence of polymers thus making such systems highly
attractive in applications such as enhanced oil recovery, detergent formulations and drug transport [40]. Some specific examples of such systems include the formation of gels, i.e. solutions of very high viscosity; as a result of the polyelectrolyte effect (repulsion between charged centers along the polymer chain causes the polyelectrolyte to adopt an extended conformation thus increasing solution viscosity). Such gels are of particular interest in the food and pharmaceutical industries, however, current patent literature indicates an increase in their use in the cosmetic and detergent industries.

The addition of either a neutral polymer or an oppositely charged polyelectrolyte (Fig. 1.11) is observed to cause a reduction in the critical micelle concentration of ionic surfactants [64]. This also results in a reduction in the surfactant monomer concentration, a factor associated with the reduction of skin irritation due to surfactants. Therefore, such combinations have significant implications for the development of ‘milder’ skin-care production formulations. The addition of surfactant (specifically sodium dodecylsulfate) to drug tablet formulations has been shown to prolong the time of release of a drug when the tablets contain the polymer hydroxypropyl-cellulose [66]. The observed prolongation of release has been due to the formation of a viscous gel layer around the tablet in an aqueous medium. Thus, possibility of tailoring systems, through the appropriate combination of surfactant and polymer, is of great scientific interest and points to the necessity of developing a clear understanding of the nature

Fig. 1.11: Illustration of the interaction of the surfactant molecules and micelles with the oppositely charged polyelectrolyte (Source: E.B. Abuin, J.C. Scaiano, J. Am. Chem. Soc. 106 (1984) 6274–6283).
of surfactant-polymer interactions in aqueous solutions under a variety of conditions. This understanding is of crucial importance with respect to any possible application, not simply drug delivery systems, in order to allow for some prediction of resulting solution properties. Unfortunately, because of complex nature of the surfactant-polymer systems, they are not yet well understood [40]. The complexity of the problem is due to the similarities involved in the solubilization of polymers in aqueous solution, and in the aggregation processes of surfactants in solution. The hydrophobicity of the polymer plays a significant role in dictating the solubility of the neutral polymer in solutions. In case of a surfactant, the net effect of various interactions such as ionic, hydrophilic and hydrophobic governs the aggregation process. However, the micellar and interfacial properties of the surfactant solutions are also influenced by the presence of a neutral polymer.

The nature of the polymer and the surfactant both play an important role in the strength of the observed interactions. In case of ionic polymers, strong electrostatic interactions are observed between polymers and surfactants of opposite charge (Fig. 1.11), while little or no interaction is observed between polymers and surfactants having like charges. The primary electrostatic binding mechanism is further reinforced by the aggregation of the alkyl tails of the bound surfactant through hydrophobic interactions [67]. In the case of neutral polymers one must consider how the addition of the polymer affects the aggregation process of the surfactant in solution, which is also governed by a balance of interactions. In addition to attractive interactions, electrostatic repulsive interactions between the ionic head groups of the surfactant molecules also occur. But the presence of the polymer tends to decrease the repulsive interactions and will give rise to net favorable interactions. This interaction also will be influenced by factors such as temperature, the presence of additional components (e.g. salt, another surfactant), the structure and charge of the surfactant, as well as the size, concentration and the structure of the polymer. In addition, any self-aggregation behavior of the polymer itself will be important [68].

Anionic surfactants interact with neutral-polymer to a greater extent than cationic surfactants as reported by Brackman and Engberts [68–70]. This difference is due to size and hydration of the head groups. In case of cationic surfactants, the bulky alkyl trimethylammonium (\(\text{RTA}^+\)) group shields the core of the micelle from getting in contact with water and thus acts like a barrier [71]. Furthermore, an unfavorable contribution to the free energy of formation of polymer-bound micelles is produced as a result of steric repulsions between the head groups and the polymer chains. Due to low mammalian toxicity of cationic surfactants in
general, and quaternary ammonium surfactants in particular, cationic surfactants are used to a large extent in a number of pharmaceutical, biomedical and personal care product applications [72]. In many cases the formulations of these products also include polymeric compounds. Due to these reasons, interactions between cationic surfactants and neural polymers as well as determining the methods of enhancing such interactions are of great practical importance. In addition, because of better performance and cost effectiveness, mixtures of surfactants are preferred over a single surfactant in most of the industrial applications [73–75]. The micelles thus formed, called ‘mixed micelles’ normally show different characteristics than their individual components. Thus, the functionality and properties of mixed micelles can be fine tuned by variation in the composition of either component. Hence, it is important to understand the way in which each surfactant interacts in mixtures and affects the nature of the mixed micelles.

References