Chapter–I

General Introduction
Surfactants and their classification

"Surfactants", a happy and convenient contraction of "surface active agents", owe their name to their interesting behaviour at surfaces and interfaces. When present at low concentration in a system, they have the property of adsorbing onto the surfaces or interfaces of the system and the adsorption of surfactants lowers the interfacial tension between phases. Because of their ability to lower interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents and so forth.

A surfactant molecule consists of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and one which is insoluble (the lyophobic part). When the fluid is water these parts are known as the hydrophilic and hydrophobic, respectively. The hydrophilic part is referred to as the head group and the hydrophobic part as the tail (Figure 1.1).

![Figure 1.1: Schematic illustration of a surfactant monomer.](image)

Most of the surfactants have a long hydrocarbon tail that can be linear or branched and interacts only very weakly with the water molecules in an aqueous environment. The hydrophilic head is a relatively small ionic or polar group that
interacts strongly with water via dipole-dipole or ion-dipole interactions. Hence, a surfactant can be said to have a *split personality*, as it is composed of two parts with entirely different tendencies. Because of this unusual amphipathy property, surfactants are very versatile substances.

Surfactants are widely used in both industry and everyday life, and the properties of the surfactant aqueous solutions have received considerable attention. Recently, the aggregation phenomenon of amphiphiles in non-aqueous media has been the scope of many researchers due to the increasing use of these materials in applications which require water-free or water-poor media [1]. The solvents used in these studies are strongly polar with water resembling properties, such as ethylene glycol, formamide, or glycerol [2-9]. Most surfactants used in practical applications are mixtures [10, 11]. Surfactant mixtures are commonly utilized in many surfactant formulations and practical applications because mixtures often behave synergistically and provide more favorable, or desirable, properties than the constituent single surfactants [12].

**Classification of surfactants**

The surfactant's hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain, the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as:
1. **Anionic surfactant:** The surface-active portion of the molecule bears a negative charge.

   *Example:* Sodium dodecyl sulphate
   
   \[ \text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+ \]

2. **Cationic surfactant:** The surface-active portion of the molecule bears a positive charge.

   *Example:* Cetyltrimethylammonium bromide
   
   \[ \text{CH}_3(\text{CH}_2)_{15}(\text{CH}_3)_3\text{N}^+\text{Br}^- \]

3. **Zwitterionic surfactant:** Both positive and negative charges are present in the surface active portion.

   *Example:* N-dodecyl-\(N,\text{N}\)-dimethylglycine
   
   \[ (\text{CH}_3)(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^- \]

4. **Nonionic surfactant:** The surface active portion bears no apparent ionic charge.

   *Example:* Polyoxyethylene 20 cetyl ether (Brij58)
   
   \[ \text{C}_{16}\text{H}_{33}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{–OH} \]

5. **Gemini surfactant:** Gemini or dimeric surfactants are the surfactants that have two hydrophilic groups and two hydrophobic groups per molecule, rather than the single hydrophilic and the single hydrophobic group of conventional surfactants (Figure 1.2). Their surface properties were first described by Mitsui Okahara of Osaka University and his colleagues [13-17], who synthesized them in their laboratories.
Compared with conventional surfactants, dimeric surfactants (gemini surfactants) are more efficient in lowering surface tension and have a much lower critical micelle concentration \((CMC)\) and better wetting properties [18-27]. They possess specific rheological and some specific aggregation properties [24, 28-34]. Therefore, it is not surprising that today they are widely used as effective emulsifiers, bactericidal agents, dispersants, antifoaming agents, detergents, etc. An important feature of these surfactants is the ability to design their physicochemical properties, supramolecular structure, and biodegradability by changing the nature and size of the spacer and alkyl chains. The general structure of the gemini surfactant is shown in Figure 1.2.

![Figure 1.2: Schematic representation of gemini surfactant.](image)

**Micelle formation**

One of the most characteristic properties of amphiphilic molecules is their capacity to aggregate in solutions. The aggregation process depends, of course, on the amphiphilic species and the condition of the system in which they are dissolved. The narrow concentration range over which surfactant solutions show an abrupt change (Figure 1.3) in physicochemical properties is called the critical concentration for the formation of micelle or 'critical micelle concentration' \((CMC)\) [35-37].
Term CMC was established by Bury [38], defining it as a concentration range below which surfactant is in solution as monomer and above which practically all additional surfactant added to the solution form micelles.

Figure 1.3: Variation of physical properties with surfactant concentrations.
Just above the CMC, micellar structure is considered to be roughly globular or spherical [39, 40]. A schematic representation of such a structure is given in Figure 1.4.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{micelle_structure.png}
\caption{Model of hypothetical ionic micelle showing the locations of headgroups, surfactant chains and counterions. Curved arrows symbolize the liquid – hydrocarbon – like nature of the core.}
\end{figure}
Figure 1.4 is a useful model for qualitative understanding of experimental results. Hydrophobic cores of micelles have diameters of about 10-30 Å. The charged coat of ionic micelles, called the Stern layer, is usually 60-90% neutralized by counter ions in aqueous surfactant solutions without added salt [40]. The surface charge of ionic micelles results in an electrical potential on the order of 100 mV at the micellar-water interface with the same sign as the surfactant head group [41]. If salt is added to the solution, the surface potential is partly neutralized. This decreases coulombic repulsion between adjacent head groups and allows the formation of larger micelles. A solution having a single, very narrow, distribution of micellar sizes is often called monodisperse. As concentrations of surfactant or salt (or both) in water are increased, globular micelles gradually turn into larger, rodlike micelles. Under some experimental conditions, spherical and rodlike micelles coexist in the same solution, such systems containing two (or more) distinct distributions of micellar sizes are called polydisperse. At higher concentrations of surfactant or salt, rodlike micelles begin to predominate. Finally, at very high surfactant concentrations, lamellar liquid crystal phases may be formed [40].

Not all surfactants form micelles in water. Depending on structure, some surfactants disperse in water as lamellar liquid crystal phases or vesicle. The practical results are that water-soluble, single chain surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium bromide, and polyoxyethylene alcohols
form micelles in water. Double-chain surfactants such as didodecyldimethylammonium bromide, dihexadecylphosphate, and many phospholipids are insoluble in water and do not form micellar structures.

Factors affecting the value of the critical micelle concentration

Since the properties of solutions of amphiphiles change markedly when micelle formation commences, a great deal of work has been done on elucidating the various factors that determine the concentration at which micelle formation becomes significant (i.e., CMC), especially in aqueous media.

Among the factors known to affect the CMC markedly in aqueous solutions are

1. Structure of amphiphiles
2. Presence of various additives in the solution
3. Experimental conditions such as temperature, pH, pressure, solvent, etc.

1. Structure of amphiphiles: In general, the CMC decreases as the hydrophobic character of the surfactant increases, i.e., CMC decreases as the number of the carbon atoms in the hydrophobic group increases. In aqueous medium ionic surfactants have much higher CMC’s than non-ionic surfactants containing equivalent groups. Zwitterionic surfactants appear to have about the same CMC’s as ionics with the same number of carbon atoms in hydrophobic group. The CMC increases as the head group is closer to the two branches of the chain partially shielding one another, interfacial energy effects are smallest. In aqueous medium,
the CMC's of ionic surfactants decrease with decrease in the hydrated radius of the counterion. When the hydrophobic group is branched, the carbon atoms on the branches appear to have about one-half the effect of carbon atoms on a straight chain [42]. When carbon-carbon double bonds are present in the hydrophobic chain, the CMC is generally higher than that of the corresponding saturated compound, with the cis isomer generally having a higher CMC than the trans isomer. This may be the result of a steric factor in micelle formation. Surfactants with either bulky hydrophobic or bulky hydrophilic groups have large CMC values than those with similar, but less bulky, groups. The increase in the CMC upon introduction of a bulky hydrophobic group in the molecule is presumably due to the difficulty of incorporating the bulky hydrophobic group in the interior of a spherical or cylindrical micelle.

2. Presence of various additives in the solutions:

(a) Effect of electrolyte: In solutions of increasing ionic strength, the forces of electrostatic repulsion between head groups of an ionic micelles are considerably reduced, enabling micelles to form more easily, that is, at lower concentration. In other words, addition of electrolyte to ionic surfactants causes CMC [43], the effect being more pronounced for anionic and cationic than for zwitterionic surfactants, and more pronounced for zwitterionics than for nonionics. The effect of the concentration of electrolyte is given by equation [43]

\[
\log CMC = -a \log C_i + b
\]  

(1.1)
where \( a \) and \( b \) are constants for a given ionic head at a particular temperature and \( C_i \) is the total (monovalent) counterion concentration in mole per dm\(^3\). The depression of the \( CMC \) in these cases is due mainly to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent decreased electrical repulsion between them in the micelle. For sodium laurate and sodium naphthenate, the order of decreasing effectiveness of the anion in depressing the \( CMC \) is \( \text{PO}_4^{3-} > \text{B}_4\text{O}_7^{2-} > \text{OH}^- > \text{CO}_3^{2-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- \) [44].

For nonionics and zwitterionics, equation (1.1) does not hold. Instead, the effect is given by the equation [45]

\[
\log CMC = -K C_S + \text{constant} \quad (C_S < 1) \tag{1.2}
\]

where \( K \) is a constant for a particular surfactant, electrolyte and temperature and \( C_S \) is the concentration of electrolyte in mole per dm\(^3\).

The change in the \( CMC \) of nonionics and zwitterionics on the addition of electrolyte has been attributed [46, 47] mainly to the "salting out" or "salting in" of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant. Salting in or salting out by an ion depends upon whether the ion is a water structure breaker or a water structure maker.

**b) Effect of organic additives:** Organic compounds affect the \( CMC \) either by penetrating into the micellar region, or by modifying solvent-micelle or solvent-monomer interactions. Non-polar compounds, such as hydrocarbons, that are
believed to penetrate into the inner portion of the core, decrease the CMC only slightly. Addition of longer chain alcohols promotes micelle formation and lowers the CMC. The magnitude of CMC decrease depends on the alkyl chain length of the organic additive and the hydrophilic group associated with the chain. Urea, formamide, and guanidinium salts are believed to increase the CMC of surfactants in aqueous solution because of their disruption of the water structure. These water structure breakers may also increase the CMC by increasing the entropy effect accompanying micellization.

3. Experimental conditions:

(a) Temperature: Temperature increase causes decreased hydration of the hydrophilic group, which favours micellization. However, temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavours micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. From the data available, the minimum in the CMC – temperature curve appears to be around 25 °C for ionics [48] and around 50 °C for nonionics [49, 50]. For bivalent metal alkyl sulphates, the CMC appears to be practically independent of the temperature [51].

(b) pH: When amphiphile molecules contain ionizable groups such as –NH₂, –(CH₃)₂N→O and –COOH, the degree of dissociation of the polar group will be dependent on pH [52]. In general, the CMC will be high at pH values where the
group is charged (low pH for \(-\text{NH}_2\) and \(-(\text{CH}_3)_2\text{N}->\), high pH for \(-\text{COOH}\)) and low when uncharged. Some zwitterionic surfactants become cationic at low pH, a change that can be accompanied by a rapid rise in the \(CMC\) [53], or a more modest rise [54] depending on the structure and hence hydrophilicity of the zwitterionic form.

(c) Pressure: Many reports have appeared on the effect of pressure on micelle formation of ionic [55-60] and non-ionic amphiphiles [61]. With pressure, \(CMC\) of ionic surfactants increases up to 1000 atm followed by a decrease above this pressure [62-67]. Such behaviour has been rationalized in terms of solidification of the micellar interior, increased dielectric constant of water [63], and other aspects related to water structure [64]. For non-ionic amphiphiles, the \(CMC\) value increases monotonously and then levels off with increasing pressure.

(d) Solvent medium: In ethylene glycol, the \(CMC\) of surfactants decreases as the length of the hydrophobic chain increases, but the change is much smaller than that in water [68] for polyoxyethylenated non-ionic solutions in benzene and carbon tetrachloride, \(CMC\)'s decrease with increase in the length of the polyoxyethylene group at constant hydrophobic chain length.

The \(CMC\)'s in benzene for alkylammonium carboxylates increase with increase in the length of the alkyl chain of the anion but decrease with increase in the length of the alkyl chain of the cation; in carbon tetrachloride, there is no significant change in the value of the \(CMC\) with these structural changes. The
CMC is lower in D₂O than H₂O for different amphiphiles [69, 70]. The hydrophobic bonds are expected to be stronger in D₂O than H₂O [71]. Also, micelles in D₂O are larger than H₂O [72].

Thermodynamics of micelle formation

Thermodynamic analysis of the micellization is based on two models:

1. Phase-separation model

2. Mass-action model

In the phase-separation model the micelles are considered to form a separate phase at the CMC, while in mass-action model, micelles and unassociated monomers are considered to be in association-dissociation equilibrium. In both of these treatments the micellization phenomenon is described in terms of the classical system of thermodynamics. The application of the mass-action and phase-separation models to both ionic and nonionic micellar systems are described below:

1. Phase-separation model

According to this model, micelles and counterions are treated as separate phase. However, the micelles do not constitute a “phase” according to the true definition of this concept since they are not homogeneous and uniform throughout. Similarly, there are problems associated with the application of the phase rule when considering micelles as a separate phase [73].
(a) Application of the phase-separation model to non-ionic surfactants

To calculate the thermodynamic parameters for the process of micellization a primary requisite is to define the standard state. The hypothetical standard state for the surfactant in the aqueous phase is taken to be the solvated monomer at unit mole fraction with the properties of the infinitely dilute solution. For the surfactant in the micellar state, the micellar state itself is considered to be the standard state.

If \( \mu_s \) and \( \mu_m \) are the chemical potentials per mole of the unassociated surfactant in the aqueous phase and associated surfactant in the micellar phase, respectively, then since these two phases are in equilibrium

\[
\mu_s = \mu_m
\]  \hspace{1cm} (1.3)

For non–ionized amphiphile,

\[
\mu_s = \mu_s^0 + RT \ln a_s
\]  \hspace{1cm} (1.4)

At low concentration of free monomers, the activity of surfactant monomer, \( a_s \), may be replaced by the mole fraction of monomers \( X_s \), and equation (1.4) becomes

\[
\mu_s = \mu_s^0 + RT \ln X_s
\]  \hspace{1cm} (1.5)

where \( \mu_s^0 \) is the chemical potential of standard state.

Since the micellar state is in its standard state

\[
\mu_m = \mu_m^0
\]  \hspace{1cm} (1.6)

If the \( \Delta G_m^0 \) is the standard free energy for the transfer of one mole of amphiphile from the solution to micellar phase, then
\[ \Delta G_m^0 = \mu_m^0 - \mu_s^0 = \mu_m - \mu_s + RT \ln X_s = RT \ln X_s \quad (1.7) \]

Assuming that the concentration of free surfactant in the presence of micelle is constant and equal to the CMC value, \(X_{CMC}\), then

\[ \Delta G_m^0 = RT \ln X_{CMC} \quad (1.8) \]

\(X_{CMC}\) is the CMC expressed as a mole fraction, therefore,

\[ X_{CMC} = \frac{n_s}{n_s + n_{H_2O}} \quad (1.9) \]

Since the number of moles of free surfactant, \(n_s\), is small compared to number of moles of water, \(n_{H_2O}\), therefore, equation (1.9) can be written as

\[ X_{CMC} = \frac{n_s}{n_{H_2O}} \quad (1.10) \]

Substituting the value of equation (1.10) into the equation (1.8) and applying logarithm we get

\[ \Delta G_m^0 = 2.303RT (\log CMC - \log w) \quad (1.11) \]

where \(w = \text{mol dm}^{-3} \text{water} \) (55.40 mol dm\(^{-3}\) at 20 °C).

Application of Gibbs–Helmholtz equation to equation (1.8) gives

\[ \frac{\partial}{\partial T}(\Delta G_m^0/T)_p = -R(\partial \ln X_{CMC}/\partial T)_p = -\Delta H_m^0/T^2 \quad (1.12) \]

Hence the standard enthalpy of micellization per mole of monomer, \(\Delta H_m^0\), is

\[ \Delta H_m^0 = -RT^2(\partial \ln X_{CMC}/\partial T)_p = R \left( \partial \ln X_{CMC}/\partial (1/T) \right)_p \quad (1.13) \]

Also, standard entropy of micellization per mole of monomer, \(\Delta S_m^0\), is given by

\[ \Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T \quad (1.14) \]
(b) Application of phase separation model to ionic surfactants

In the calculation of $\Delta G^0_m$, it is necessary to consider not only the transfer of surfactant molecules from the aqueous to micellar phase but also the transfer of $(1-\alpha)$ moles of counterion from its standard state to the micelle. Therefore, equation (1.7) can be written as

$$\Delta G^0_m = RT \ln X_s + (1-\alpha) RT \ln X_x \quad (1.15)$$

where $X_s$ and $X_x$ are the mole fractions of surfactant ions and counterions, respectively.

The analogous equations (1.8) and (1.11) for an ionic surfactant in the absence of added electrolyte are

$$\Delta G^0_m = (2 - \alpha) RT \ln CMC \quad (1.16)$$

$$\Delta G^0_m = (2 - \alpha) 2.303RT (\log CMC - \log w) \quad (1.17)$$

It is assumed that micellar phase is composed of the charged aggregates together with an equivalent number of counterions, and equations (1.16) and (1.17) are approximated to

$$\Delta G^0_m = 2RT \ln X_{CMC} \quad (1.18)$$

$$\Delta G^0_m = 4.606RT (\log CMC - \log w) \quad (1.19)$$

The enthalpy of micellization $\Delta H^0_m$, for ionic surfactants is given by

$$\Delta H^0_m = -2RT^2 (\delta \ln X_{CMC} / \delta T)_P$$
One of main criticism of phase separation model is that it predicts that the activity of the monomer above the CMC remains constant. Surface tension and emf measurements indicate decrease in monomer activity above CMC for ionic surfactants.

2. Mass-action model

In the mass-action model, it is assumed that associated and unassociated surfactant ions are in association-dissociation equilibrium and micellization is considered as a reversible process. The mass-action model was originally applied to ionic surfactants but latter it was applied to nonionic surfactants also.

(a) Application of the mass-action model to non-ionic surfactants

Micelles, $M$, are considered to be formed by a single step reaction from $n$ monomers, $D$,

$$nD \rightleftharpoons M$$ \hspace{1cm} (1.21)

The equilibrium constant for micelle formation, $K_m$, is then given by

$$K_m = a_m / \langle a_i \rangle^n$$ \hspace{1cm} (1.22)

Corkill et al. [74] have shown that at the CMC the standard free energy of micellization, $\Delta G_m^0$, is given by

$$\Delta G_m^0 = RT \left( (1-1/n) \ln X_{CMC} + f(n) \right)$$ \hspace{1cm} (1.23)

where

$$f(n) = \frac{1}{n}[\ln^2(2n-1/n-2) + (n-1)\ln(2n-1)/2(n^2-1)]$$ \hspace{1cm} (1.24)
If $n$ is large, equation (1.23) reduces to

$$\Delta G_m^0 = RT \ln X_{\text{CMC}}$$

(1.25)

Applying the Gibbs-Helmoltz equation and assuming the aggregation number, $n$, to be large and independent of temperature

$$\Delta H_m^0 = -RT \left( \frac{\partial \ln X_{\text{CMC}}}{\partial T} \right)_P = R \left( \frac{\partial \ln X_{\text{CMC}}}{\partial (1/T)} \right)_P$$

(1.26)

The aggregation numbers of many non-ionic surfactants vary with temperature and in some cases a concentration dependence of $n$ has been reported. In such cases equation (1.26) is not applicable.

(b) Application of mass-action model to ionic surfactants

The ionic micelles, $M^\text{+p}$, is considered to be formed by the association of $n$ surfactant ions, $D^+$, and $(n-p)$ firmly bound counterions, $X^-$.

$$nD^+ + (n-p)X^- \rightleftharpoons M^\text{+p}$$

(1.27)

The equilibrium constant for micelle formation assuming ideality, is thus,

$$K_m = X_m/(X_\text{CMC})^n (X_\text{CMC})^{n-p}$$

(1.28)

where $X_x$ is the mole fraction of counterion.

The standard free energy of micellization per mole of monomeric surfactant is given by

$$\Delta G_m^0 = -RT/n \ln K_m = -RT/n \ln X_m/(X_\text{CMC})^n (X_\text{CMC})^{n-p}$$

(1.29)

When the aggregation number, $n$, is large, and when data in the region of the CMC are considered, equation (1.29) becomes

$$\Delta G_m^0 = (2 - p/n)RT \ln X_{\text{CMC}}$$

(1.30)
equation (1.30) is of the same form as equation (1.16) from the phase-separation model, since \( \alpha = p/n \). The two equations differ slightly because of differences in the way in which the mole fractions are calculated. In the phase-separation model the total number of moles present at the CMC is equal to the sum of the moles of water and surfactant whereas the total number of moles in the mass-action model is equal to the sum of the moles of water, surfactant ions, micelles, and free counterions.

The standard enthalpy of micellization (per mole of monomer) is given by

\[
\Delta H_m^0 = -(2 - \alpha) R T^2 \left( \partial \ln X_{\text{CMC}} / \partial T \right)_P
\]

\[= (2 - \alpha) R \left[ (\partial \ln X_{\text{CMC}} / \partial (1/T))_P \right]
\]

(1.31)

The mass-action model is more realistic model than the phase-separation model in describing the variation of monomer concentration with total concentration above the CMC.

Both the mass-action and phase-separation models, despite their limitations, are useful representations of the micellar process and may be used to derive equations relating the CMC to the various factors that determine it.

**Other thermodynamic models**

The thermodynamics of small systems developed by Hill [75] has been applied to non-ionized, non-interacting surfactant systems by Hall and Pethica [76]. In this approach, aggregation number is treated as thermodynamic variable, thereby enabling variations in the thermodynamic functions of micelle formation.
with the mean aggregation number, \( <n> \), to be examined. The thermodynamic functions of micellization assuming solution ideality are as under

\[
\Delta G_m^0 = RT \left[ \ln X_s - \frac{1}{<n>} \ln X_m </n> \right] \tag{1.32}
\]

\[
\Delta H_m^0 = -RT^2 \left[ (d\ln X_s/dT)_P - 1/<n> (d\ln X_m/dT)_P \right] \tag{1.33}
\]

\[
\Delta S_m^0 = -RT \left( d\ln X_s/dT \right)_P + RT/<n> (d\ln X_m/dT)_P - R \ln X_s + (R/<n>) \ln X_m \tag{1.34}
\]

For systems where \( <n> \) is large and changes little with temperature, equations (1.32) to (1.34) are reduced to the corresponding equations of mass-action or phase-separation models.

Another approach for that of small systems was formulated by Corkill and coworkers and applied to systems of non-ionic surfactants [77, 78]. This multiple equilibrium model considers equilibria between all micellar species present in solution rather than a single micellar species, as was considered by mass-action theory. The standard free energy and enthalpy of micellization are given by equations of similar form to equations (1.32) and (1.33) and are shown to approximate satisfactorily to the appropriate mass-action equations for systems in which the mean aggregation number exceeds 20.

An interesting model of micelle formation based on geometrical considerations of micelle shape has been proposed by Tanford [79]. Equations are presented which relate the micelle size and CMC to a size-dependent free energy of micellization. The calculations are based on the assumptions of an
ellipsoidal shape. The hydrophobic component of the free energy is estimated in terms of the area of contact between the hydrophobic core and the solvent. The hydrophilic component of $\Delta G_m^0$, i.e., the free energy of repulsion between the head groups, is assumed to be inversely proportional to the surface area per head group. This approach has been further developed by Ruckenstein and Nagarajan [80] and used in the prediction of the properties of sodium octanoate micellar solutions [81].

**Micellar aggregation numbers**

An important property of micelle formation is the mean aggregation number which provides direct information about the general size and shape of the aggregates formed by amphiphiles in solution, and how these properties are related to the molecular structure of the amphiphiles. The mean aggregation number refers to the number of surfactant monomers that, on average, assemble to form a super molecular structure, i.e., a micelle. The most common shape of micellar aggregates in solution is spherical, and hence these are the most extensively studied. The main driving force for the self-assembly of surfactant monomers into micelles is to minimize the hydrocarbon-water contacts in solution. For this reason, the lower limit of the number of surfactant monomers that form a micelle is dictated by the minimum number that must come together to effectively shield one another from contact with water [82].

From geometric considerations, the aggregation number $N_{agg}$ of micelles in aqueous media should increase rapidly with increase in the length of the
hydrophobic group $l_c$ of the surfactant molecule and decrease with increase in the cross-sectional area of the hydrophilic group $a_0$ or the volume of the hydrophobic group $V_H$.

Ionic surfactants containing a single long alkyl chain and zwitterionics (containing a single long alkyl chain) in which the electrical charges are not on adjacent atoms show aggregation numbers of less than 100 in aqueous solutions containing low or moderate concentrations of NaCl ($\leq 0.1$M), and these vary only slightly with the surfactant concentration up to about 0.1-0.3M [83]. This is indicative of spherical micelle formation. At high salt content, however, $n$ increases sharply with surfactant concentration [84], with formation of rodlike cylindrical or disklike lamellar micelles. The formation of rodlike micelles and the sharp increase in aggregation number result in an increase in the viscosity of the aqueous solution [85].

In the case of non-ionic surfactants, steric effect as well as a preference for the hydration of the head group opposes micelle formation [82]. Micelle formation, therefore, represents a cooperative process, whereby a number of surfactant monomers come together through a compromise of opposing forces. It is important to note that micelles are not "monodisperse" in nature, i.e., they do not have a uniform size of a fixed number of monomers. Rather there exists a distribution of aggregate sizes from which the average number of monomers contained in a micelle is taken as the mean aggregation number, $N_{agg}$. 
In polar solvents, such as chloroform or ethanol, micellization does not occur or, if it does, the aggregation number is very small, presumably because the polar surfactant molecules can dissolve in the solvent without distorting its liquid structure significantly. As might be expected, in these solvents, surfactants have also almost no tendency to adsorb at the interfaces.

**Mixed micellization**

The amphiphilic molecules have a tendency to collect at any interface where the hydrophobic groups can be partially or completely removed from the contact of water and the hydrophilic groups remain wetted. This dual tendency of the molecules, as we know, results in the formation of the micelles.

The formation of micelles from more than one chemical species gives rise to what is known as mixed micelles. Micelles may be formed from the compounds which are either heterodisperse or polydisperse, and Gibbons [86] had identified important difference between the two types of compounds. Nemethy and Ray [87] have taken advantage of this important property of polydisperse compounds in a thermodynamic study of micelle formation by nonionic surfactants in ethylene glycol-water mixtures. Another class of mixed micelles results when low molecular weight molecules are solubilized by micelles formed from surfactants containing a relatively larger nonpolar side chain. The solubilized substance, also called a penetrating additive [70], may be located in the hydrocarbon core [88] or hydrophilic mantle [89]. Several studies have been concerned with this aspect of
micelle formation [90]. The surface properties of ionic micelles have been shown to be altered by mixed micelle formation. Tokiwa and Ohki [91] have shown that the addition of an anionic surfactant increases the apparent dissociation constant of micelles of a cationic-nonionic surfactant, and the addition of a cationic surfactant produces the opposite effect. The degree of counterion binding by mixed micelles formed from anionic and nonionic surfactants was found to decrease as the proportion of the nonionic component increased. It was also found to depend upon the length of the nonionic polyoxyethylene head groups [92]. These observations can be understood in terms of an altered charge density at the micelle surface as a result of mixed micelle formation, and possible interaction between the anionic and nonionic head groups. The latter has been demonstrated by NMR studies [93, 94] in which the aromatic portion of the anionic surfactant shifts the proton resonance signal of the polyoxyethylene group upfield.

From application point of view, mixed micelles are often used in technical, pharmaceutical, and biological fields, since they work better than pure micelles [12, 95]. They have importance in industrial preparation, pharmaceutical and medicinal formulation, enhanced oil recovery process, and so forth, by way of efficient solubilization, suspension, dispersion, and transportation influenced by temperature, pressure, pH, nature of solvent, additives, etc. [96].
**Theories of mixed micellization**

A mixed micelle is one, which is composed of surfactant molecules of more than one type. Interest in mixed micelles has largely been driven by industry, in search of properties that lie beyond that defined by each surfactant component. Such a synergistic effect greatly improves many technological applications in areas such as emulsion formulation, interfacial tension reduction, cosmetic products, pharmaceuticals, and petroleum recovery, etc. In this regard, the specific interaction between two components of a mixture on their physicochemical properties including the adsorption behaviour and micellization is of paramount importance. Various theoretical models have been proposed to interpret the formulation of mixed micelles (composition and interaction parameter) and monolayer formation. The first model given by Lange [97] and used by Clint [98], is based on phase separation model and assumes ideal mixing of the surfactant in the micellar phase. Rubingh [99] proposed a treatment based on regular solution theory for non-ideal mixed systems which has been extensively used [100, 101]. Motomura et al. [102] proposed a thermodynamic method to describe the mixed micellar thermodynamic properties as functions of excess thermodynamic quantities. More recently, Rodenas et al. [103] used a simple theoretical treatment, based on Lange’s model that utilizes the Gibbs-Duhem equation to relate the activity coefficients of the surfactants in the mixed micelles. Maeda [104] introduced a term, $G_{\text{mix}}$, as a measure of stability of mixed systems. Attempts by other workers [105-108] have been made to predict the properties and
interactions in binary surfactant systems, particularly remarkable in this respect are the efforts recently carried out by the Blankschtein’s group [106, 109-113], who proposed a molecular-thermodynamic approach as a valuable tool to predict solution properties of mixed surfactant systems. Apart from this, Rosen et al. [114-116] have extended the non-ideal solution treatment of Rubingh [99] for mixed micelle formation by binary surfactant systems to estimate, from surface tension data, the surfactant molecular interactions and also the composition in the adsorbed mixed monolayer at the air/water interface.

**Importance of research problem**

“Gemini surfactants” have structures and properties, which are different from those of monomeric surfactants and are said to be “unique to the world of surfactants”. These surfactants show high surface activity, unusual viscosity changes with an increase in [surfactant], a low critical micelle concentration (CMC), and unusual micellar structures. Cationic gemini surfactants have wide applications because of their excellent surface activity. They are used as hair conditioners and fabric softeners. They are also used in foaming, agrochemical spreading aids, and cleaning processes.

Many studies have been focused on the properties and micellization behaviour of gemini surfactants, such as critical micelle concentration (CMC), surface tension, and the various aggregation behaviour [29]. Usually, the additives can improve the desired properties of surfactant solutions. The most widely used additives are alcohols and amines.
Alcohols are known to play important roles as co-surfactants in a number of industrial and research applications including the addition of alcohol to surfactant and oil systems in order to form microemulsions [117-124]. Microemulsions are added to oil reservoirs to enhance recovery by mobilizing some of the residual oil that remains after extraction. Amines are also used as co-surfactants for microemulsion formulations with surfactant + oil systems [125, 126]. Further, microemulsions are considered to be good drug carriers and the presence of amines in such combinations may show their specific effects [127] as blood and saliva are known to contain various amines and polyamines [128].

The purpose of my present study is to find out the effect of various amines/alcohols additives on the gemini surfactants, which can further be used for drug encapsulation and delivery. Thus, the experimental results of my present study may be useful in understanding and predicting the surfactants selection for controlled drug release targeted delivery.
Layout of the thesis

This thesis consists of the following four chapters:

Chapter-I: General Introduction.

Chapter-II: Experimental.

Chapter-III: Surface and Solution Properties of Cationic Gemini Alkanediyl-α, ω-bis(dimethylcetylammonium bromide) Surfactants (16-s-16, s = 4, 5, 6) with Alcohols: Tensiometric and Fluorometric Studies.

(A): Interactions between Cationic Gemini Alkanediyl-α, ω-bis(dimethylcetylammonium bromide) Surfactants (16-s-16, s = 4, 5, 6) and Primary Linear Alcohols.

(B): Interactions between Cationic Gemini Alkanediyl-α, ω-bis(dimethylcetylammonium bromide) Surfactants (16-s-16, s = 4, 5, 6) and Alcohols (1,2-Butandiol, 2-Methyl-1-butanol, 2-Ethyl-1-butanol, 2-Butene-1,4-diol).

Chapter-IV: Mixed Micellization between Cationic Gemini Alkanediyl-α, ω-bis(dimethylcetylammonium bromide) Surfactants (16-s-16, s = 4, 5, 6) and Amines: A Tensiometric Study.

(A): Interactions between Cationic Gemini Alkanediyl-α, ω-bis(dimethylcetylammonium bromide) Surfactants (16-s-16, s = 4, 5, 6) and Primary Linear Alkyl Amines.

(B): Interactions between Cationic Gemini Alkanediyl-α, ω-bis(dimethylcetylammonium bromide) Surfactants (16-s-16, s = 4, 5, 6) and Ethyleneamines (Ethylenediamine, Diethylenetriamine, Triethylenetetramine, Tetraethylenepentamine).
References:


Chapter–II

Experimental