CHAPTER I

General Introduction
1.1 Surfactants, classification and properties

Surfactants are surface-active molecules and the necessary criterion for a molecule to behave as a surfactant is that it should have the dual nature of hydrophobicity and hydrophilicity. In general, these two behaviours are called solvophobicity and solvophilicity of a surfactant. A surfactant molecule therefore contains a solvophobic part of sufficient length and a solvophilic end. The solvophobic part consists of hydrocarbon chain with eight or more carbon atoms, which is simply called 'tail' and the solvophilic part is called 'head'. The solvophobic part may consist of more than one hydrocarbon chains also. Due to the dual nature of surfactants, these molecules are also called amphiphiles.

Surfactants can be broadly classified as biosurfactants and synthetic surfactants. Naturally occurring surfactants are called biosurfactants, which are found in biological systems. Examples are phospholipids, fatty acids and bile salts. Synthetic surfactants are synthesized for specific domestic or industrial uses. Detergents are formulations containing mainly synthetic surfactants as active components. Both natural and synthetic surfactants are further classified as anionic, cationic, nonionic and zwitterionic.

Anionic surfactants can be represented by the general formula $\text{RA}^\text{−}\text{M}^+$, where $\text{R}$ is the hydrophobic chain with $\text{A}^\text{−}$ head group and $\text{M}^+$ is the counter ion. When dissolved in polar solvents, they dissociate to give negatively charged monomeric species and the corresponding counter ions. They aggregate to give anionic micelles. Sodium dodecyl sulfate (SDS; $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}^+$) and sodium
alkyl benzene sulfonate ($RC_6H_4SO_3^-$) are some of the widely used anionic surfactants. Cationic surfactants have the general formula $RX^+Y^-$, which dissociate in polar solvents to give positively charged surfactant moiety and negatively charged counter ions. They form cationic micelles. Examples of cationic surfactants are cetyl trimethylammonium bromide (CTAB; $CH_3(CH_2)15N^+(CH_3)3Br^-$) and cetyl pyridinium chloride (CPC; $C_{16}H_{33}C_5H_4N^+Cl^-$).

Nonionic surfactants do not carry any electrical charge and hence their aggregates do not have any surface charge. Polyoxyethylene (23) dodecanol (brij 35), polyoxyethylene (9-10) octyl phenol (Triton X–100) and polyoxyethylene (20) sorbitan monooleate (Tween 80) are some well known nonionic surfactants. Zwitterionic surfactants possess both anionic and cationic groups on the hydrophobic moiety and can behave as anionic, cationic or neutral species depending on the pH of the medium. N-alkyl and C-alkyl betaines, phosphatidyl amino alcohols and acids are examples of such surfactants.

Conventional surfactants have one head group attached to one hydrocarbon chain (single-chained) or two hydrocarbon chains (double-chained) or even three hydrocarbon chains (triple-chained). Hydrocarbon chains may be branched also. There is a new class of synthetic surfactants having remarkable surface-active properties and these surfactants are called gemini surfactants. Gemini surfactant molecules contain two head groups and two hydrocarbon chains. The two hydrocarbon chains are connected through another hydrocarbon chain known as spacer. The surfactant is called gemini or dimeric when the spacer is between the
two head groups and bolaform if the spacer is between the hydrocarbon chains. The length of the spacer can be varied by varying the number of carbon atoms and nature of the spacer governs the properties of these surfactants. In view of the immense importance and application of surfactants, continuous efforts are going on to synthesize newer surfactants with special properties, for e.g., photo-sensitive surfactants.3-5

Surfactants, due to their amphiphilic nature, possess two important properties. These are (i) surface activity or adsorption at an interface and (ii) self-organization or aggregation in a given medium. Surfactants, due to their adsorbing ability, lower the surface tension of a solution and form monolayers, films and multilayers. On the other hand, surfactants form, due to their self-organizing ability, aggregates like micelles, vesicles and membranes. Adsorption and aggregation abilities of surfactant molecules are responsible for their applications in various fields.

1.2 Thermodynamics of adsorption

Equilibrium exists between surfactant molecules at the interface and those in the bulk solution. The change in surface Gibbs function, \( dG_s \) at constant temperature and pressure is given as

\[
dG_s = \gamma d\sigma + \sum I \mu_i d\eta_{i\sigma}
\]  

(1.1)

where \( \gamma \) is the surface tension, \( d\sigma \) is the change in the area of the surface, \( \mu_i \) is the chemical potential of the \( i^{th} \) component and \( d\eta_{i\sigma} \) is the change in the amount of the
i\textsuperscript{th} component at the interface. In the light of the thermodynamic principles, we obtain the relation

\[ d\gamma = -\sum_i \Gamma_i d\mu_i \]  

(1.2)

where \( d\gamma \) is the change in the surface or interfacial tension of the solvent and \( d\mu_i \) is the change in chemical potential of the \( i\text{th} \) component. \( \Gamma_i \) is the surface excess of the \( i\text{th} \) component and is defined as

\[ \Gamma_i = n_i / \sigma \]  

(1.3)

\( n_i \) and \( \Gamma_i \) can be positive or negative. Eq. (1.2) is known as the **Gibbs adsorption isotherm**. For a two-component system at constant temperature and pressure Eq. (1.2) reduces to

\[ d\gamma = -\Gamma_1 d\mu_2 - \Gamma_2 d\mu_2 \]  

(1.4)

Subscripts 1 and 2 refer to solvent and solute, respectively. The location of the dividing surface of the two bulk phases is arbitrarily chosen such that the surface excess concentration of the solvent, \( \Gamma_1 \), becomes zero. This is, in fact, the most realistic position since we are considering a surface layer of adsorbed solute. Eq. (1.4) now becomes

\[ d\gamma = -\Gamma_2 d\mu_2 = -RTa_2 d\ln a_2 \]  

(1.5)

where \( a_2 \) is the activity of solute, \( R \) is the gas constant and \( T \) is the temperature. For dilute solutions \( a_2 \) can be replaced by the concentration term \( a_2 \). For a surfactant solution, we can now write the Gibbs adsorption isotherm as

\[ \Gamma = -\left( \frac{1}{RT} \right) \frac{d\gamma}{d\ln c} \]  

(1.6)
where $c$ and $\Gamma$ are the concentration and surface excess of the surfactant, respectively. Since $\Gamma$ is positive for surfactants, $\frac{dy}{d\ln c}$ must be negative. Therefore, accumulation of surfactants on the surface or interface lowers the surface tension. In surfactant solutions the surface tension initially decreases with increasing surfactant concentration and then attains generally a constant value above a critical concentration.

Eq. (1.6) is, however, found to be valid in the case of nonionic surfactants only. For ionic surfactants, Gibbs adsorption isotherm has a form different from Eq. (1.6), which was discussed in detail by Prosser and Franses.\(^6\) We consider here an anionic surfactant BM in aqueous medium in the presence of an added electrolyte XM. The Gibbs adsorption isotherm given by Eq. (1.2) can be written in the expanded form for the solution containing RM and XM as

$$\frac{dy}{d\ln c} = -RT[\Gamma_M d\ln c_M + \Gamma_B d\ln c_B + \Gamma_X d\ln c_X] \quad (1.7)$$

where $\Gamma_M$, $\Gamma_B$ and $\Gamma_X$ are the surface excess of ionic species $M^+$, $B^-$ and $X^-$, respectively. We have considered here symmetric univalent surfactant and added electrolyte only. Let $c$ and $c_e$ be the bulk concentrations of surfactant and electrolyte, respectively. If $\Gamma$ and $\Gamma_e$ are the surface excess of surfactant and electrolyte, respectively, then for a combination of univalent surfactant and electrolyte, Eq. (1.7) takes the form

$$\frac{dy}{d\ln c} = -RT[\ln(c + c_e) + d\ln c] \quad (1.8)$$
In the absence of an electrolyte, for surface excess of a symmetric univalent surfactant one gets from Eq. (1.8) an expression of the type

\[ \Gamma = -\left(\frac{1}{2RT}\right)\left(\frac{dy}{d\ln c}\right) \]  

Equation (1.8) on differentiation and further rearrangement yields an expression for the surface excess of a univalent surfactant in the presence of a particular concentration of 1:1 electrolyte, which is of the form

\[ \Gamma = -\left(\frac{1}{RT}\right)\left[\frac{1}{1+c+ce}\right]\left(\frac{dy}{d\ln c}\right)ce \]  

1.3 Thermodynamics of aggregation

The second important property of a surfactant is its ability to undergo aggregation. Aggregation of a surfactant in solution is commonly known as micellization and the aggregates are called micelles. The surfactant concentration in a given medium at which surfactant molecules start aggregating to form micelles is known as the critical micelle concentration (cmc). Two approaches are used to understand the thermodynamics of the micellization, which are phase - separation and mass - action models. These two models are briefly discussed below.

1.3.1 Phase – separation model

In this model the micelle is treated as a separate phase. 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.\(^7\)

If \(\mu_s\) and \(\mu_m\) are the chemical potential of the unassociated surfactant in the aqueous phase and of the associated surfactant in the micellar phase, respectively, and since the two phases are in equilibrium at and above the \(\text{cmc}\),

\[
\mu_s = \mu_m \quad \text{(1.11)}
\]

For a non-ionized surfactant, assuming the concentration of free monomers to be low, we get

\[
\mu_s = \mu_s^0 + RT\ln X_s \quad \text{(1.12)}
\]

\(\mu_s^0\) corresponds to the chemical potential at the standard state and \(X_s\) is the concentration of surfactant monomers in mole fraction. Since micellar phase is treated as a separate hydrocarbon phase, the mole fraction of the associated surfactant in this phase is equal to one and therefore

\[
\mu_m = \mu_m^0 \quad \text{(1.13)}
\]

If \(\Delta G_{\text{mic}}^0\) is the standard free energy change for transfer of one mole of surfactant from solution to micellar phase, then

\[
\Delta G_{\text{mic}}^0 = \mu_m^0 - \mu_s^0 = \mu_m - \mu_s + RT\ln X_s = RT\ln X_s \quad \text{(1.14)}
\]

Assuming that the concentration of free surfactant in the presence of micelle is constant and equal to the critical micelle concentration, we get \(X_s = X_{\text{cmc}}\). Eq. (1.14) therefore becomes

\[
\Delta G_{\text{mic}}^0 = RT\ln X_{\text{cmc}} \quad \text{(1.15)}
\]
In the case of ionic surfactants, $\Delta G_{\text{mic}}^0$ must also include the free energy change for the transfer of $\beta$ moles of counter ion from its standard state in the solution phase to the micellar phase. $\beta$ is the number of moles of counter ion per mole of the associated monomer in the micellar phase and is known as the counter ion binding constant. If one mole of micelle consist of $n$ mole of surfactant and $m$ moles of counter ion, $\beta = m/n$. $n$ is generally known as aggregation number. It is also considered that the free counter ions present in the solution phase are in equilibrium with the counter ions bound to the micelle. For ionic surfactants Eq. (1.15) therefore modifies to

$$\Delta G_{\text{mic}}^0 = RT\ln X_{\text{cmc}} + \beta RT\ln X_c$$

(1.16)

Where $X_c$ is the mole fraction of counter ion in the solution. At the cmc when the micellar phase is just formed, in the absence of added electrolyte it can be approximated that $X_c = X_{\text{cmc}}$ and Eq. (1.16) becomes

$$\Delta G_{\text{mic}}^0 = (1 + \beta)RT\ln X_{\text{cmc}}$$

(1.17)

1.3.2 Mass–action model

In this model applicable to ionic surfactants, micelles are assumed to be in equilibrium with the surfactant monomer ions and counter ions. Further it is assumed that micelles are effectively monodispersed. The equilibrium is represented as

$$nB^- + mM^+ \rightleftharpoons A^{(n-m)-}$$

(1.18)
In the above equilibrium, $B^-$, $M^+$ and $A^{(n-m)^-}$ represent single detergent ion, counter ion and anionic micelle, respectively. Applying the mass-action law to the above equilibrium, the corresponding equilibrium constant, $K$, can be written as

$$K = \frac{a_A}{a_B a_M}$$  \hspace{1cm} (1.19)

$a_A$, $a_B$ and $a_M$ are activities of the surfactant monomer, counter ion and micelle, respectively. The standard free energy of micellization per mole of surfactant monomer is given by

$$\Delta G^0_{\text{mic}} = -\frac{RT}{n} \ln K$$  \hspace{1cm} (1.20)

Substituting the value of $K$ from Eq. (1.20), we get near cmc after substituting concentration for activity and ignoring the term $\ln c_A/n$

$$\ln \text{cmc} = \frac{\Delta G^0_{\text{mic}}}{RT} - \beta \ln c_M$$  \hspace{1cm} (1.21)

$c_M$ is the concentration of the counter ion. Eq. (1.21) is known as the Corrin–Harkins equation.  

1.4 Micellization parameters

Micellization behaviour of surfactants is characterized and quantified in terms of different parameters, which are known as micellization parameters. A brief account of the most commonly used micellization parameters are given below.

1.4.1 Critical micelle concentration

The critical value of a surfactant concentration at which micellization starts is known as its critical micelle concentration (cmc) as mentioned above in section 1.3. When micelle forms, sudden change in several physical properties of surfactant
solutions takes place enabling us to determine experimentally values of cmc. Normally, changes in physical properties like surface tension, conductivity, viscosity, solubilization, osmotic pressure, etc, take place over a narrow concentration range. Therefore, a precise determination of the cmc is difficult and moreover values of cmc estimated from different experimental methods may also differ to a certain extent. Thus, numerous methods are available for determining the value of cmc. Tensiometry, conductometry, fluorimetry and calorimetry are some of the commonly used methods.

Critical micelle concentration is an important property of a surfactant, which reflects on its micellization ability. Smaller the cmc better is the surfactant. Cmc of a surfactant is affected by several factors. It is dependent on the number of carbon atoms in the hydrocarbon chain of the surfactant. As the number of carbon atoms increases cmc decreases. The dependence of cmc on the number of carbon atoms beyond 16 is not very significant. Branching of the hydrocarbon chain also affects the cmc. Nature of hydrophilic group is another factor on which cmc shows strong dependence. There is a pronounced difference between the cmc’s of ionic and nonionic surfactants with identical hydrophobic moieties indicating the influence of hydrophilic head group on cmc. The lower cmc’s of the nonionic surfactants are a consequence of the lack of electrical work necessary in forming the micelles. Nature of counter ion, its radius and valence, also largely affect the value of cmc of ionic surfactants. Cmc has interesting temperature dependence. Most of the ionic surfactants exhibit at some temperature a
minimum in the cmc.\textsuperscript{18,19,25,28} This property of ionic surfactants is used in the
differential scanning calorimetry technique for studying the micellization behaviour
of ionic surfactants.\textsuperscript{29} With increase in pressure cmc of ionic surfactants in water
show a maximum.\textsuperscript{30-37} Added electrolytes have significant effect on the cmc of both
ionic and nonionic surfactants.\textsuperscript{11-17,25,38-45} Non-electrolytes like urea, amides,
alcohols, etc on addition produce both increase and decrease of cmc of
surfactants.\textsuperscript{46-53}

1.4.2 Aggregation number

Aggregation number is another important fundamental parameter
concerning a micelle and it is equal to the number of monomers present in a
micelle. It gives an idea about the size of a micelle. It is determined using
experimental techniques like dynamic light scattering (DLS), small-angle neutron
scattering (SANS), steady-state fluorescence quenching and time-resolved
fluorescence quenching.\textsuperscript{39,55-61} Some of the factors affecting aggregation number are
structure of a surfactant, concentration of surfactant,\textsuperscript{56,60-62} concentration of added
electrolyte,\textsuperscript{41-43,52,61-65} counter-ion binding constant, nature of solvent, etc.
Significant changes in aggregation number lead to micellar shape transition. In a
micellar solution, all micelles may not have same aggregation number and poly-
dispersity exists.\textsuperscript{66} However, for the sake of simplicity such polydispersity is
generally ignored for calculation purpose and only monodispersed micelles with
single aggregation number are taken into account.
1.4.3 Counter ion binding constant

In the case of ionic surfactants, counter ion binding constant is an important parameter. As mentioned above in section 1.3.1, counter ion binding constant (\( \beta \)) is equal to the number of moles of counter ion bound to the ionic micelle divided by the aggregation number. \( \beta \) is always found to be less than one thereby signifying presence of residual electric charge on the surface of an ionic micelle. Counter ion binding ability is one of the important characteristics of ionic micelles. Counter ions control not only the critical micelle concentration (cmc) and aggregation number (\( N_{agg} \)) of ionic surfactants, but also the reactions\(^6\) that take place in the presence of ionic surfactants. The shape of an ionic micelle appears to have an influence on the value of \( \beta \). In non-aqueous polar solvent media, \( \beta \) generally has a lower value than in water.

Due to the presence of effective electric charge on the ionic micelle, an electric potential is developed at the surface of the ionic micelle, which is known as surface potential of the ionic micelle. The surface potential value controls different processes that take place near the micelle – solution interface.

1.5 Shape and structure of micelles

Micelles are aggregates of surfactant monomers and the aggregated species are in dynamic equilibrium with the monomers. Therefore, considering micelles to have rigid structures with precise shapes may be unrealistic. However, SANS, DLS and phase diagram studies made on micellar solutions support the concept of micelles having regular shapes. It is assumed that near the cmc micelles are roughly...
spherical. The radius of a micelle cannot be greater than the stretched-out length of the surfactant molecule. Typically micelles may have average radii of 1.2 – 3 nm and can contain 20 – 100 monomers. Added electrolyte has great influence on the shape of ionic micelles. As the counter ion concentration is increased, the shape of ionic micelles is reported to change from spherical to non-spherical shapes like ellipsoidal, cylindrical, hexagonal, etc.

The interior of a micelle consists of a liquid core, which is oil like, formed by the associated hydrocarbon chains. In ionic micelle the charged head groups project out into the water phase. Similar structure of micelles exists in polar non-aqueous solvents also. In non-polar solvents the structure of micelle gets reversed. The region immediately surrounding the core is the Stern layer, which contains the ionic head groups and a part of counter ions (bound counter ions). The Stern layer constitutes the inner part of the electrical double layer surrounding the micelle. The outer layer, which is a diffuse layer contains the remaining counter ions (free counter ions) and is known as Gouy-Chapman layer.

1.6 Scope of the work

Hydrophobic interaction is a type of water – solute interaction where the solute has either full or partial hydrophobicity. Similarly, hydrophilicity is also due to water – solute interaction. These interactions responsible for hydrophobicity and hydrophilicity are not water specific and exist in other solvents also. Therefore, solvophobicity and solvophilicity are the general terms used. When the solutes are amphiphilic in nature, solvophobic interaction leads to two significant phenomena,
viz. adsorption and aggregation. Thus, adsorption and self-organization of surfactants take place only in the presence of a solvent. Solvents therefore play a decisive role in controlling the adsorption and micellization characteristics of surfactants. For instance, solvophobicity of the tail part of a surfactant towards one solvent can change over to solvophilicity in another solvent. Consequently, a particular surfactant may form normal micelles, no micelles or reverse micelles by changing the polarity of solvent. Recent works of Eastoe and coworkers illustrate the profound effects of solvent properties on aggregation and adsorption of surfactants. For example, Seguin et al. showed that in a mixed solvent containing ethylene glycol (EG) and propylene glycol (PG) the aggregation of nonionic surfactants can be switched ‘on’ or ‘off’ by controlling the EG:PG ratio. Despite extensive studies made on the micellization behaviour of surfactants in different types of media, it is still not exactly clear which property of a solvent controls the micellization process, although hydrogen bonding between the solvent molecules is considered to be a prerequisite for aggregation of surfactants. Moreover, quantifying solvophobicity and solvophilicity is still an unsettled problem. Studying the adsorption and aggregation behaviours of surfactants in different solvents of varying property therefore provides useful information of fundamental and practical importance. The different solvent media used for such study are (i) water in the absence and presence of various types of additives that alter the water structure, (ii) non-aqueous polar solvents including ionic liquids, (iii) mixed solvents containing water and organic polar solvent, and (iv) non-polar
organic solvents. Continued studies on the adsorption and micellization behaviours of surfactants in organic polar solvents and their aqueous mixtures indicate the importance and relevance of such studies.\textsuperscript{61,68-111}

In view of the above points, we have undertaken in this thesis a study on the adsorption and aggregation of ionic surfactants in binary mixed solvents containing water as one of the components.

The reported results about the cmc of SDS in water + acetamide medium based on conductance method are not consistent.\textsuperscript{112,113} Therefore, in chapter 3 we have made a detailed study on the adsorption and micellization of SDS in water + acetamide medium by using surface tension, conductance and fluorescence methods.

Normally, cmc of a surfactant in organic polar solvent is more than that in water. But for sodium dioctylsulfosuccinate (AOT)\textsuperscript{89,90} in water + EG and water + formamide (FA) media unusual trends in the variation of cmc with increase in the amount of organic solvent were reported. The reported cmc values of AOT in pure EG and FA are even lower than that in water, which is contradictory to the normal trend. Similarly, inconsistent cmc values were reported\textsuperscript{80,81,91,102} for SDS in water + FA media using conductance method. The reported trend in the variation of cmc of SDS with increase in the amount of FA is also contradictory to the normal trend.

Furthermore, on surveying the literature,\textsuperscript{73,103,114} we found that the micellization behaviour of CPC, a commonly used cationic surfactant, has not been studied in water + EG and water + FA mixed solvent media covering the entire composition.
range, i.e., from 0 to 100 % of EG or FA. Therefore, in chapter 4 we investigated the adsorption and aggregation behaviours of AOT and CPC in water + EG media, while in chapter 5 we investigated the adsorption and aggregation behaviours of AOT, CPC and SDS in water + FA media.
References


