CHAPTER-I

General Introduction
Surface and interfaces

The terms 'surface' and 'interface' are two familiar words for physical chemists. Although both are boundary between any two immiscible phases such as gas/liquid, liquid/liquid, or solid/liquid, the term (surface) is used only in the first case, that is, to deal with a boundary between the gas (usually air)/liquid. Because of difference in physical, chemical and electrical properties of matter at these boundaries from those of the same matter in bulk, two different situations may arise. First one is the case in which the contribution of these abnormal properties at interfaces to general properties and behaviour of the system is negligible as the fraction of total mass localized at the boundaries is so small. The second case is that in which the properties at these boundaries play a significant, sometimes a major, role. In this case, surfactant is expected to play a main role. Examples for such circumstances are when (i) the phase boundary area is so large relative to the volume of the system that a substantial fraction of the total mass of the system is present at boundaries (as in emulsions, foams and dispersions of solids, etc.) or (ii) the phenomena occurring at phase boundaries are so unusual relative to the expected bulk phase interactions that the entire behaviour of the system is determined by interfacial processes (as in heterogeneous catalysis, corrosion, detergency, and flotation, etc.).
Surfactants, classification and properties

**Surfactants**, a convenient contraction of 'SURFace ACTive AgeNTS', are the surface-active molecules and necessary criterion for a molecule to behave as a surfactant is that it should have amphiphilic character or dual nature (solvophobicity and solvophilicity) on dispersing in a solvent. When water is used as solvent, generally, the terms hydrophobicity and hydrophilicity are used to explain various processes. For convenience, structurally, surfactant molecules can be divided into two parts – a nonpolar hydrophobic portion which is called as tail and a polar hydrophilic portion called as head. The tail part may consist of one or more hydrocarbon chains, usually with 6-22 carbon atoms. The chains may be linear or branched, may contain unsaturated portions or aromatic moieties, and may be partly or completely halogenated (as in fluorocarbon surfactants) while a charged or uncharged hydrophilic species (group) acts as the head part of the molecule.

![Schematic representation of a surfactant monomer.](image)

**Figure 1.1:** Schematic representation of a surfactant monomer.

Due to the dual nature of surfactant molecules, they are also called as amphiphiles (coined by Paul Winsor) – the term which was derived from the two
Greek words *amphi* (double) and *philos* (affinity). The ambivalence of amphiphiles towards an aqueous environment leads to phenomena which solutions of simpler solute molecules and water do not exhibit. That is, the amphiphilicity of surfactant molecules leads them into two characteristic properties, viz. adsorption (surface activity) at an interface and aggregation (self-association) in a given medium. Adsorption causes for the lowering of surface tension and forms monolayers, films and multilayers. The formation of different types of aggregates like micelles, vesicles and membranes is due to the self-association capability of the surfactants. In a suitable solvent, usually water, they form different type of aggregates in which the hydrophobic moieties are shielded from water and the solvated hydrophilic moieties being located at the surface of the aggregate.\(^1\)\(^2\) The adsorption and self-association abilities of the surfactant molecules are responsible for their application in various fields.

Surfactants are the most versatile products of the chemical industry and they are used in many practical applications/areas such as catalysis, paints and coatings, dispersions, electronics, flotation of minerals, lubrication, textile industry, agrochemicals, fibers, cosmetics, pharmaceuticals, leather technology, photography, laundering and general cleaning uses, preparation of inks and pigments, petroleum and paper industries, etc. For most industrial chemists, as they (surfactants) find applications in almost every chemical industry, a fundamental understanding of their unusual properties and phase behaviour is
necessary. In addition, an understanding of the basic phenomena involved in the application of surfactants, such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting, spreading and adhesion, etc., is of vital importance in arriving at the right composition and control of the system involved. This is particularly the case with many formulations in the chemical industry.

Surfactants may be classified according to their particular uses such as soaps, detergents, wetting agents, foaming agents, corrosion inhibitors, etc., or by the structure they are able to build, as for example, membranes, microemulsions, vesicles, liposomes, etc., or based on their origin as biosurfactants (naturally occurring surfactants which are found in biological systems—examples: phospholipids, fatty acids and bile salts, etc.), and synthetic surfactants (surfactants which are synthesized for the specific domestic or industrial uses). However, the most accepted classification is based on their dissociation in water i.e., ionicity. Here, one sees whether the surfactant is charged or uncharged, ionic or nonionic? The classification is as follows:

**Ionic surfactants**

An ionic surfactant, on dissolution in water, results in a surface-active portion that has a net charge. Ionic surfactants can further be classified as cationic, anionic and zwitterionic depending on whether the head group is positively, negatively or positively & negatively charged.
**Cationic surfactants:** The most prevalent cationic surfactants are based on quaternary ammonium, imidazolinium, or alkylpyridinium compounds. Although less numerous, phosphorus can also be quaternized with alkyl groups to provide alkyl phosphonium bromides. Here the surface active head group portion bears a positive charge.

*Examples:*

Hexadecyltrimethylammonium bromide $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$

Hexadecylpyridinium chloride $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+\text{C}_5\text{H}_5\text{Cl}^-$

**Anionic surfactants:** Alkalialkanoates are the most common anionic surfactants. They also include traditional soaps ($\text{RCOO}^-\text{Na}^+$), sulphonates ($-\text{SO}_3^-$) and sulphates ($-\text{OSO}_3^-$), etc. Here the surface active head group portion bears a negative charge.

*Examples:*

Sodium laurate $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-\text{Na}^+$

Sodium dodecylbenzene sulfonate $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3^-\text{Na}^+$

**Zwitterionic surfactants:** This type of surfactants can behave as cationic, anionic or nonionic species, depending upon the pH of the solution. Both positive and negative charges are present in the surface active portion.
Examples:

3-(Dimethyldodecylammonio)-propane-1-sulfonate $\text{CH}_3(\text{CH}_2)_{11}N^+(\text{CH}_3)\text{2}(\text{CH}_2)\text{3SO}_3^-$

$N$-Dodecyl-$N,N$-dimethyl betaine $\text{CH}_3(\text{CH}_2)_{11}N^+(\text{CH}_3)\text{2CH}_2\text{COO}^-$

Nonionic surfactants

As their name implies, nonionic surfactants contain only electrically neutral head groups. Ethoxylates (alkylethyleneoxide surfactants) which are generally represented as $\text{C}_n\text{E}_m$, where ‘$n$’ is the number of methylene groups in the alkyl chain and ‘$m$’ is the number of ethylene oxide units in the head group, are the prevalent nonionic surfactants. Here, the surface active portion bears no apparent ionic charge, but has a polar head group (containing hydroxyl groups or polyoxyethylene chains).

Examples:

Polyoxyethylene monohexadecyl ether $\text{CH}_3(\text{CH}_2)_{15}(\text{OCH}_2\text{CH}_2)_{21}\text{OH}$

Polyoxyethylene octylphenylether $\text{C}_{14}\text{H}_{22}\text{O(C}_2\text{H}_4\text{O})_{9,5}$

In a conventional surfactant, the head group is connected to single hydrocarbon chain or double hydrocarbon chains (sometimes even triple hydrocarbon chains). The hydrocarbon chains may be branched also.
**Bolaform surfactants**

Bolaform surfactants consist of two hydrophilic head groups, connected by a long, linear polymethylene chain (Figure 1.2). Their self-association ability is less, compared to conventional ionic surfactants. However, they show biological activity and some special bolaforms are capable of giving rise to organized assemblies of peculiar structure.

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

**Examples:**

- Hexadecanediyl-1,16-bis(trimethylammonium bromide) \( (\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{16}\text{N}^+(\text{CH}_3)_2\text{Br}^- \)

- Potassium hexadecanedioate \( \text{O}_2\text{C(\text{CH}_2)_{14}\text{CO}_2}^-\text{K}^+ \)

**Gemini (dimeric) surfactants**

One of the most exciting developments in the field of surfactant chemistry is the emergence of the Gemini (dimeric) surfactants. The term ‘Gemini surfactant’, coined by Menger, has become accepted in the surfactant literature for describing dimeric surfactants, that is, surfactant molecules containing two hydrophobic groups and two hydrophilic groups, connected by a linkage (spacer)
close to hydrophilic groups. A schematic representation of a gemini surfactant is shown in Figure 1.3.

![Schematic representation of a gemini surfactant](image)

**Figure 1.3: Schematic representation of a gemini surfactant.**

Geminis were known long before to Bunton et al., who studied catalysis of nucleophilic substitutions by ‘dicationic detergents’ and to Devinsky et al., who reported the surface activity and micelle formation of some new ‘bisquaternary ammonium salts’. Later, Okahara and coworkers prepared and examined amphiphatic compounds with two sulfate groups and two lipophilic alkyl chains. Menger and Littau assigned the name ‘gemini’ to bis-surfactants with a rigid spacer (i.e., benzene, stilbene), but name was then extended to other bis or double tailed surfactants, irrespective of the nature of the spacers.

It was pointed out by Rosen that these surfactants could be more surface active by orders of magnitude than comparable conventional surfactants containing a similar single hydrophobic tail and a single hydrophilic group. As a
result, numerous papers appeared in the literature describing the fundamental properties of gemini surfactants. Among these gemini surfactants, the cationic bis(alkyldimethylammonium)alkane dibromide type, with two tails and a spacer separating the two quaternary nitrogen atoms in the heads, designated as m-s-m, where m and s refer to the carbon numbers of the side chains and of the alkanediyl spacer, has received more attention. The three structural elements- hydrophilic head group, a hydrophobic tail group, and the spacer- may be varied to change the properties of the gemini surfactants. The interest in academic circles and among scientists at surfactant-producing companies is due the following reasons:

(i) Their $CMC$ is at least one order of magnitude lower than for the corresponding single tail – single head surfactants, on a weight percent basis.

(ii) They are 10–100 times more efficient at reducing the surface tension of water and the interfacial tension at an oil/water interface than conventional surfactants.

(iii) They appear to have better solubilizing, wetting, foaming, and lime-soap dispersing ability than the conventional surfactants. Some cationic gemini surfactants possess interesting biological properties.

(iv) The aqueous solutions of some gemini surfactants with a short spacer show special rheological properties (viscoelasticity, shear-thickening) at relatively low concentration.
Gemini surfactants can be synthesized with an enormous variety of structures. In principle, it is possible to connect any two identical or different surfactants among the available ones by a spacer group that can be hydrophilic or hydrophobic, flexible or rigid, heteroatomic, aromatic, etc. This is only limited by the skill of the organic synthetic chemist. Therefore, the structures and properties of gemini surfactants can be more finely tuned for a given application than for conventional surfactants.

Although majority of the geminis have symmetrical structures (identical head and tails on both end of the spacer), unsymmetrical geminis\textsuperscript{13, 14} and gemini with three or more polar groups or tails\textsuperscript{15-17} are also known.

\textit{Micelle formation and critical micelle concentration}

One of the most characteristic properties of the surfactant molecules is their ability to aggregate in solution. When surfactants are dissolved in water, they initially minimize their free energy by creating a monolayer on the air-water surface. In this layer, the hydrophobic parts of the surfactants are directed towards less polar air, while the hydrophilic groups are directed towards the polar water molecules. As the surfactant concentration is increased, the surface becomes increasingly populated by surfactant molecules, therefore decreasing the surface tension of the solution. On further addition, beyond a critical concentration (when the surface is fully occupied), they start to aggregate leading them into a variety of structures in which the hydrophilic head groups expose towards aqueous phase.
and hydrophobic tails away from that. These aggregate structures influence the macroscopic solution properties and therefore play important roles in the performance of a wide range of industrial and consumer products, including detergents, paints, cosmetics and pharmaceuticals. The narrow concentration range over which surfactant solutions show an abrupt change in physicochemical properties (discontinuous break) is termed the critical micelle concentration (CMC)\textsuperscript{18-20} and the aggregates thus formed are called micelles.

The term CMC was established by Davis and Bury\textsuperscript{21} defining it as a concentration range below which the surfactant molecules in the solution remain as monomers and above which practically all additional surfactants added to the solution form micelles. CMC is an important property of the surfactants which reflects its micellization ability. A good surfactant will have a lower CMC value. Below the CMC, the physicochemical properties of ionic surfactants resemble to those of strong electrolytes and, above the CMC, these properties change dramatically (Figure 1.4), indicating that a highly cooperative association takes place.
Figure 1.4: Changes in the physicochemical properties of surfactant solution around the critical micelle concentration.

The aggregation of surfactants/amphiphilic compounds can be demonstrated by measuring solution properties such as surface tension,\(^{22-24}\) dye solubilization,\(^{25-27}\) \(^1\)H-NMR,\(^{28-30}\) light scattering,\(^{31-33}\) fluorimetry,\(^{34-36}\) Osmotic pressure,\(^{37-39}\) electrical conductivity,\(^{40-42}\) ultrasound velocity,\(^{43}\) against the surfactant concentration. The value of \(CMC\) depends on the measured solution properties and hence a difference in their values is often associated with different experimental techniques. This is the reason why a narrow concentration range is preferred for the \(CMC\) values.

In a micellar solution, there is always a dynamic equilibrium between the surfactant monomers, monolayers and micelles (Figure 1.5).
Figure 1.5: Surfactant existence in different phases, dependent on surfactant concentration.

**Types of micelles**

Although the exact structure of the micelle is still somewhat controversial, just above the CMC it is considered to be roughly globular or spherical.\textsuperscript{44,45} The radius of the micelle can not be greater than the stretched-out length of the surfactant molecules.

Micelles formed in polar solvents are called *normal micelles* and those formed in nonpolar solvents are called *reverse micelles*. Another type is *mixed micelle* which is formed upon mixing of two or more surfactants. All the three are briefly discussed below.
Figure 1.6: Schematic presentation of normal (A), reverse (B) and mixed micelles (C). In (C), \(\blacklozenge\) and \(\circ\) indicate different surfactant monomers.

**Normal micelles:** An ionic normal micelle may contain three regions (Figure 1.7): (i) A liquid-like hydrocarbon core (as the interior part consists of the hydrophobic hydrocarbon chains of the surfactant molecules). The radius of this core is roughly equal to the length of fully extended hydrocarbon chain (~12-30 Å). (ii) An aqueous layer surrounding the core of the micelles, called *Stern layer*. The inner part of the electrical double layer is constituted by this layer. It contains the regularly charged head groups and 60-90% of the counterions (the bound counterions). The head groups are hydrated by a number of water molecules. One or more methylene groups attached to the head group may be wet. The core and Stern layer form kinetic micelle. (iii) An outer layer which extends into further aqueous phase, called *Gouy-Chapman* layer. This layer consists of the remaining counterions. The thickness of this layer is determined by the effective ionic strength of the solution.
Figure 1.7: A two dimensional schematic representation of regions of spherical ionic micelle. The counterions (X), the head groups (○), and the hydrocarbon chains (―――) are schematically indicated to denote their relative locations but not their number, distribution, or configuration.
Reverse micelles: In a reverse micelle, head group of surfactant molecules locate inside to form a polar core and hydrocarbon tails are directed towards the bulk solvent to form the outside shell of the micelle.\textsuperscript{46-52} Dipole-dipole\textsuperscript{33,34} interactions hold the hydrophilic head groups together in the core. The water molecules are strongly associated with the head groups of surfactant. The aggregation properties of surfactants in nonpolar media are often altered markedly by the presence of traces of water or additives.

In recent years, the field of reverse micelles has witnessed a significant growth of interest, partly due to the finding that proteins, other biopolymers, and even bacterial cell can be solubilized in the reverse micellar system: in fact, this has permitted the extension of area of interest to new domains, i.e., biocatalysis and chemical biotechnology.

Mixed micelles: Mixing of two or more surfactants in solution leads to the formation of mixed micelles. A mixed micelle is an aggregate of surfactant molecules composed of different types of surfactants present in solution. They provide better performance characteristics in their applications than those consisting of only one type of surfactants.\textsuperscript{55-59} The CMC of the mixed micelles, in most of the cases, fall between the CMCs of pure components, but some times it may fall below\textsuperscript{60-62} or raise even above\textsuperscript{63-66} this range.

Generally, mixtures with similar structure show ideal mixing, while head group, hydrophobic tails and counterion modifications induce significant
nonideality. The binary combination of ionic-ionic, ionic-nonionic, and nonionic-nonionic surfactant systems including a number of bile salts and amphiphilic drugs\textsuperscript{67-69} have been studied. The theoretical approaches are found to be most successful in describing the micellar behaviour of anionic-anionic surfactant solutions. A generalized multicomponent nonideal mixed micelle model based on the pseudophase separation approach is presented by Holland and Rubingh.\textsuperscript{70} Surfactant-surfactant interactions in mixed micelles and monolayer formation were extensively studied by Rosen.\textsuperscript{71,72}

**Factors affecting the CMC of surfactants**

The factors known to affect the CMC in aqueous micellar solution markedly are structure of surfactants, presence of additives (electrolytes, nonelectrolytes, or organic solvents) in solution, temperature, pressure, pH, etc. of the system and they are briefly discussed below.

*Structure of the surfactants:* In general, the CMC decreases as the hydrophobic character of the surfactant increases. The reduction in the CMC with the increase in the tail length of the surfactant molecule is due to the enhancement in hydrophobicity. However, when the number of carbon atoms in a straight chain hydrophobic tail exceeds 16, the CMC no longer decreases rapidly with the increase in the chain length. After exceeding 18 carbon atoms, the CMC values remain substantially unchanged with further increase in the chain length due to coiling of these long chains in water.\textsuperscript{72}
The carbon atoms in a branched hydrophobic group appear to have about one half the effects of carbon atoms in straight chains. Hydrophobic groups having unsaturated bonds usually show a higher CMC than the corresponding saturated groups. Surfactants with bulky hydrophobic or hydrophilic groups show higher CMC than those with less bulky groups.

In aqueous medium, ionic surfactants have much higher CMCs than nonionic surfactants containing equivalent groups. Zwitterionic surfactants appear to have about the same CMCs as ionics with the same number of carbon atoms in the hydrophobic groups. The CMC of the ionic surfactant decreases as the hydrated radius of the counterion decreases. For usual type of polyoxyethyleneated nonionic surfactants, the CMC decreases with the decrease in the number of oxyethylene units in the polyoxyethylene chain, since this makes the surfactant more hydrophobic.

**Presence of additives in solution:** Addition of electrolytes to aqueous surfactant solutions may result in a modification of both intramicellar and intermicellar interactions. Decrease in the CMC in presence of electrolytes is due to reduced repulsion between the electrostatic head groups in the micelles enabling micelles to form more easily, i.e., at lower concentration. An increase in size of counterions decreases the CMC due to the increase in the hydrophobic character. This is the reason why \((\text{C}_3\text{H}_7)_4\text{N}^+\) is more efficient in reducing the CMC than \((\text{C}_2\text{H}_5)_4\text{N}^+,\) which is more efficient than \((\text{CH}_3)_4\text{N}^+.\)
There have been attempts to examine the salts effect on micelle formation in the light of Hofmeister (lyotropic) series.\textsuperscript{73,74} The series plays a notable role in a wide range of biological and physicochemical phenomena. However, depending on the system and type, there may be changes in order in the series. A very recent study carried out by Moulik and coworkers\textsuperscript{75} shows that, for a given anionic surfactant, the order of effectiveness in reducing the $CMC$ decreases in the order $\text{Mg}^{2+} > \text{Cs}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$. The same authors have reported two $CMC$ values for a given cationic surfactant in presence of anions like salicylate $(\text{C}_7\text{H}_5\text{O}_3^-)$, benzoate $(\text{C}_7\text{H}_5\text{O}_2^-)$, oxalate $(\text{C}_2\text{O}_4^{2-})$, tartrate $(\text{C}_4\text{H}_6\text{O}_6^{2-})$. For a given nonionic surfactant, the effect of anions on the $CMC$ follows the order $\text{F}^->\text{Cl}^->\text{SO}_4^{2-}>\text{Br}^->\text{PO}_4^{3-}>\text{C}_3\text{H}_5\text{O}(\text{COO})_2^->\text{I}^->\text{SCN}^-$ and the effect of cations follows the order $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Ca}^{2+} > \text{Al}^{3+}$.\textsuperscript{76}

Small amount of organic materials significantly influences the $CMC$ of aqueous micellar solutions. Additives like urea has been shown to increase the $CMC$ of ionic\textsuperscript{77-80} and nonionic surfactants.\textsuperscript{81-83} For fluorocarbon surfactants, addition of urea slightly decreases the $CMC$.\textsuperscript{84} Addition of alcohols produce both increase and decrease in $CMC$ of surfactants.\textsuperscript{85-89} A decrease in the $CMC$ has been observed with the increase in the carbon number of the linear alcohols (heptyl to decyl) in nonaqueous dimethylformamide.\textsuperscript{90} Introduction of sugars has been known to decrease the cmc of the system.\textsuperscript{91,92} For an ionic surfactant solution, decrease\textsuperscript{93} as well as increase\textsuperscript{94} in $CMC$ has been reported with different
concentrations of acetamide. Amines are more surface active than alcohols at air-water interface. Addition of \( n \)-alkylamines (butyl to decyl) have been found to be solubilized in micellar phase, leaving the amine group on the surface of the micelles. These solubilized amines have been reported to form mixed micelles with ionic surfactants. Studies have also been carried out in presence of certain organic solvents like ethylene glycol, glycerol, dimethyl sulfoxides, formamide, and so forth. Usually, these solvents increase the CMC of the surfactants. More discussion about this has been given under the sub-heading relevance of the research problem.

**Temperature:** The effect of temperature on the CMC of surfactants in aqueous medium is somewhat complex; the value appearing first to decrease with the temperature to some minimum and then to increase with further increase in temperature. For ionic and nonionic surfactants, the minimum in the CMC appears to be around at 25 °C and 50 °C, respectively. Data on the effect of temperature on the zwitterionic surfactants are limited. They appear to indicate a steady decrease in the CMC of alkylbetaines with increase in the temperature in the range of 6–60 °C.

**Pressure:** Many reports have appeared on the effect of pressure on the micelle formation of ionic and nonionic surfactants. Although an increase in pressure up to 1000 atm increases the CMC, beyond the above pressure a decrease in CMC is observed. Such behaviour has been rationalized in terms of solidification...
of the micellar interior, increased dielectric constant of the water and other aspects related to water structure. For nonionic surfactants, the CMC value increases monotonously and then levels off with increasing pressure.

*Counterion binding constant*

For an ionic surfactant, micelle formation is associated with two types of opposing forces: (i) removal of hydrocarbon chain from the bulk phase to micellar phase which favours the aggregation and, (ii) electrostatic repulsion between the identically charged head groups, which disfavours the process of aggregation. Counterions bound to the micellar interface can cause a screening effect to the second type of force of interaction. Therefore, counterion binding is considered as an important parameter in the process of micellization. Shapes of ionic micelles appear to have an influence on the value of counterion binding. Due to the presence of effective dielectric charge on the ionic micelles, an electric potential is developed at the surface of such micelles. The surface potential value controls different processes that take place near the micelle-solution interface. Value of counterion binding constant also gives an idea about the fraction of counterion dissociated in the micellar solution.

*Aggregation number*

Micelle aggregation number, which is the number of monomers making up the micelle, is a fundamental parameter concerning the micelle. It gives an idea
about the size of the micelle and is vital in determining the stability and practical applications of the investigated systems.\textsuperscript{1,12} It depends on different factors such as concentration of surfactant,\textsuperscript{114-117} temperature,\textsuperscript{1,118-120} concentration of added electrolyte,\textsuperscript{116,121-127} organic additives,\textsuperscript{128-130} etc. Various experimental techniques like dynamic light scattering (DLS), small-angle neutron scattering (SANS), steady-state fluorescence quenching (SSFQ), and time-resolved fluorescence quenching (TRFQ), etc. may be used for the determination of aggregation number.\textsuperscript{114-116,131-140}

In a micellar solution, all micelles may not have the same aggregation and polydispersity exists.\textsuperscript{141} However, for the sake of simplicity such polydispersity is generally ignored for calculation purposes and only monodispersed micelles with single aggregation number are taken into account.

\textit{Micellar packing parameters}

The shapes of the micelles produced in aqueous media are of importance in determining various properties of the surfactant solution, such as its viscosity, its capacity to solubilize water-insoluble materials, and its cloud point. It is known that the shape of micelles depends strongly upon the actual packing parameters in the micellar assembly.\textsuperscript{142,143} A study by Israelachvili\textsuperscript{144} developed a general theoretical frame work from which the secondary structures formed by a surfactant may be deduced based on its molecular geometry. He showed that many surfactants can be generalized into certain shape categories, which are likely to
produce specific secondary aggregates in aqueous solution. The packing parameter \( p \) determines which aggregate the surfactant is most likely to form.\(^{145}\) It is calculated by dividing the volume of hydrocarbon chains \( v \) (Table 1.1) by the cross-sectional surface area \( a_o \) of the head groups and length of the alkyl chain \( l_c \), so that the non-dimensional packing parameter \( p \) is

\[
p = \frac{v}{a_o l_c} \tag{1.1}
\]

where the tail and volume of the hydrocarbon chain of \( n_c \) carbon atoms can be approximated by correlations of experimental data as:

\[
l_c = 1.54 + 1.265n_c \text{ (Å)} \tag{1.2}
\]

\[
v = 27.4 + 26.9n_c \text{ (Å)} \tag{1.3}
\]

As shown in Table 1.1, spherical micelles are formed when \( p \) is lower than 1/3; wormlike micelles are formed when \( p \) has a value in between 1/3 to 1/2; vesicles or bilayers are formed when \( 1/2 < p < 1 \). When the volume of the hydrocarbon part is large relative to the head group area \( (p > 1) \), reverse micelles are formed.
Table 1.1: Aggregate structures with their corresponding packing parameters

<table>
<thead>
<tr>
<th>Effective Shape of the surfactant molecule</th>
<th>Packing parameter ($p$)</th>
<th>Type of aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone</td>
<td>$&lt;1/3$</td>
<td>spherical micelles</td>
</tr>
<tr>
<td>truncated cone</td>
<td>$1/3-1/2$</td>
<td>wormlike micelles</td>
</tr>
<tr>
<td>cylinder</td>
<td>$1/2-1$</td>
<td>bilayers</td>
</tr>
<tr>
<td>inverted cone</td>
<td>$&gt;1$</td>
<td>reverse micelles</td>
</tr>
</tbody>
</table>
However, it is to be noted that the Eq. (1.1) and its implications listed in Table 1.1 present only general guidelines for surfactant structures. Solution parameters such as concentration, pH, temperature and solvent polarity may heavily modify the specific structures formed.

**Thermodynamics of aggregation**

The formation of micelles in aqueous solution is viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment. A clear understanding of the process of aggregation is necessary for rational explanation of the effects of structural and environmental factors on the value of $CMC$ and for predicting the effect on it of new structural and environmental variations. The determination of the thermodynamic parameters of the micellization has played an important role in developing such an understanding. Two approaches are generally used for this purpose, which are phase--separation and mass--action models. In the phase--separation model,\textsuperscript{72,146--148} micelles are considered to form separate phase above $CMC$ and in the mass action model,\textsuperscript{72,149--152} the micelles and unassociated monomeric species are considered to be in a kind of association-dissociation equilibrium. In both these treatments, the micellization is described in terms of classical system of thermodynamics.

**Phase--separation model:** Phase--separation model has been shown to account for, at least semi-quantitatively, the observed concentration dependence of apparent
molar properties and has been useful in deriving thermodynamic functions of
micellization using both apparent and partial molar properties. In 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\textsuperscript{153} while considering micelles as
separate phase.

**Application of the phase–separation model to non-ionic surfactants:** To evaluate
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, since these two phases are in equilibrium at and above the CMC

$$\mu_s = \mu_m$$ \hspace{1cm} (1.4)

For non–ionized surfactant, assuming the concentration of free surfactant
monomers to be low, we may write

$$\mu_s = \mu_s^0 + RT \ln a_s$$ \hspace{1cm} (1.5)
where $\mu_s^0$ is the chemical potential at standard state. Since the micellar phase is treated as a separate phase, the mole fraction of the associated surfactant in this phase is equal to one and therefore

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

At low concentration of free monomers, the activity $a_s$ is replaced by mole fraction $x_s$.

If the $\Delta G_m^0$ is the standard free energy for the transfer of one mole of surfactant from the solution to micellar phase, then

$$\Delta G_m^0 = \mu_m^0 - x_s = \mu_m - (\mu_s - RT \ln x_s) = RT \ln x_s$$ \hspace{1cm} (1.7)

Assuming that the concentration of free surfactant in the presence of micelle is constant and equal to the CMC value in mole fraction scale, i.e., $x_{CMC}$, then Eq. (1.7) transforms to

$$\Delta G_m^0 = RT \ln x_{CMC}$$ \hspace{1cm} (1.8)

$$x_{CMC} = \frac{n_s}{n_s + n_{H_2O}}$$ \hspace{1cm} (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, Eq. (1.9) can be written as
\[ x_{\text{CMC}} = \frac{n_s}{n_{\text{H}_2\text{O}}} \]  

(1.10)

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

\[ \Delta G^0_m = 2.303RT(\log\text{CMC} - \log w) \]  

(1.11)

where \( w \) is the number of moles of water (55.56 mol dm\(^{-3}\) at 25 \(^0\)C).

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

\[ \frac{\partial}{\partial T}\left(\frac{\Delta G^0_m}{T}\right)_p = -R\left(\frac{\partial \ln x_{\text{CMC}}}{\partial T}\right)_p = \frac{\Delta H^0_m}{T^2} \]  

(1.12)

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

\[ \Delta H^0_m = -RT^2\left(\frac{\partial \ln x_{\text{CMC}}}{\partial T}\right)_p = R\left(\frac{\partial \ln x_{\text{CMC}}}{\partial (1/T)}\right)_p \]  

(1.13)

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

\[ \Delta S^0_m = \left(\frac{\Delta H^0_m - \Delta G^0_m}{T}\right) \]  

(1.14)

**Application of phase–separation model to ionic surfactants:** In the calculation of \( \Delta G^0_m \), it is necessary to consider the transfer of \((1 - g)\)moles of counterions (where \( g \) is the degree of counterion dissociation) from its standard state to micellar state.
in addition to transfer of surfactant molecules from the aqueous phase. Therefore, Eq. (1.7) can be written as

$$\Delta G_m^0 = RT \ln x_s + (1 - g)RT \ln x_c$$

(1.15)

where $x_s$ and $x_c$ are the mole fractions of surfactant ions and counterions, respectively.

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

$$\Delta G_m^0 = (2 - g)RT \ln x_{CMC}$$

(1.16)

$$\Delta G_m^0 = (2 - g)2.303RT(\log CMC - \log w)$$

(1.17)

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

$$\Delta G_m^0 = 2RT \ln x_{CMC}$$

(1.18)

$$\Delta G_m^0 = 4.606RT(\log CMC - \log w)$$

(1.19)

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

$$\Delta H_m^0 = -2RT \left( \frac{\delta \ln x_{CMC}}{\delta T} \right)_p$$

(1.20)
One main criticism of phase separation model is that it predicts constant activity above *CMC*, which, however, was found to remain constant. Surface tension and emf measurements indicate decrease in monomer activity above *CMC* for ionic surfactant.

**Mass-action model:** In this 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 later it was applied to nonionic surfactants also.

**Application of the mass-action model to non-ionic surfactants:** The mass action model is more appropriate description of the micellar process as it considers the *n* monomers of surfactant S and micelles M to be in equilibrium with one another, i.e.,

\[ nS \rightleftharpoons K_m \rightarrow M \]

where *K*m is the equilibrium constant, and is given by

\[ K_m = \frac{[M]}{[S]^n} = \frac{a_m}{(a_S)^n} \]  

(1.21)

Assuming ideality, we can write

\[ K_m = \frac{x_m}{(x_S)^n} \]  

(1.22)

The free energy of micellization at the *CMC* is given by
\[ \Delta G_m^0 = RT \left[ \left(1 - \frac{1}{n}\right) \ln x_{\text{CMC}} + f(n) \right] \] (1.23)

where

\[ f(n) = \frac{1}{n} \left[ \ln n^2 \left(\frac{2n-1}{n-2}\right) + (n-1) \ln \frac{n(2n-1)}{2(n^2-1)} \right] \] (1.24)

If \( n \) is large, Eq. (1.23) reduces to

\[ \Delta G_m^0 = RT \ln x_{\text{CMC}} \] (1.25)

Application of the Gibbs–Helmholtz equation to Eq. (1.25) gives

\[ \Delta H_m^0 = -RT \frac{\partial \ln x_{\text{CMC}}}{\partial T} = R \frac{\partial \ln x_{\text{CMC}}}{\partial (1/T)} \] (1.26)

**Application of the mass-action model to ionic surfactants:** The ionic micelle \( M^{\pm \pm} \) is considered to be formed by the association of \( n \) surfactant ions, \( S^+ \), and \( (n-p) \) firmly bound counterions, \( X^- \)

\[ nS^+ + (n-p)X^- \rightleftharpoons M^{\pm \pm} \]

The equilibrium constant for micelle formation, assuming ideality, may be written as

\[ K_m = \frac{x_m}{(x_x)^n(x_y)^{n-p}} \] (1.27)

where \( x_x \) is the mole fraction of counterion.
The standard free energy of micellization per mole of monomeric surfactant is given by

\[ \Delta G_m^0 = -\frac{RT}{n} \ln K_m = -\frac{RT}{n} \ln \frac{x_m}{(x_s)^n(x_p)^{n-p}} \]  

(1.28)

At CMC, the above equation reduces to (assuming \( n \) is large)

\[ \Delta G_m^0 = \left(2 - \frac{p}{n}\right)RT \ln x_{CMC} \]  

(1.29)

Since \( g = \frac{p}{n} \), the above equation is same as Eq. (1.16) obtained from phase separation model.

The standard enthalpy of micellization (per mole of monomer) may be written as

\[ \Delta H_m^0 = -RT^2(2 - g) \left(\frac{\partial \ln x_{CMC}}{\partial T}\right)_p \]

The mass action model is more realistic model than the phase separation model in describing the variation of monomer concentration with total concentration above CMC. However, it suffers a serious limitation in that it considers monodispersity of micelle size inspite of polydispersity. The phase separation model assumes constant surfactant activity and hence surface tension above CMC although neither of them remains constant. If aggregation number \( n \) is infinite then mass action and phase separation models are equivalent.
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. Neither mass action nor phase separation models are enough to explain the thermodynamics of micellization completely. The thermodynamic parameters are determined either by calorimetry or by measuring CMC at different temperatures but the results, often, don’t agree well. So it is clear from the above discussion that more reliable data are necessary to overcome the present difficulties in the quantitative interpretation of micellization and also should be aware of limitations and analyze findings in terms of appropriate models.

Relevance of the research problem

Self-aggregation of surfactants takes place only in presence of a solvent. The solvophobicity of the tail part of a surfactant molecule towards one solvent can change over to solvophilicity in another solvent. Consequently, a particular surfactant may form normal micelle, reverse micelle, or no micelle by changing the polarity of the solvent. Hence, the solvents play a decisive role in controlling the micellization characteristics of the surfactants. Organic solvents are often used along with surfactants especially for pharmaceuticals, personal care products, and paint formulations. The surfactants typically serve as a carrier of active ingredients whereas cosolvent imparts beneficial qualities (examples, viscosity, volatility, etc.)
to the formulations. Thus the investigation of effects of organic solvents on the aggregation of surfactants is of considerable practical interest.

Water being the most prominent fluid on earth, extensive studies have been reported on the micellization of various kind of surfactants in aqueous medium at different conditions. Indeed, micellization has been observed in a variety of solvents whose polarity lies either lower or higher than that of water. Apart from the pure solvents, the study of micelle formation in mixed solvents containing water is also of considerable interest both from fundamental and applied viewpoints. To understand the aggregation in mixed solvents, it becomes necessary to understand how a range of compositions of solvent mixtures influences the micelle formation, as the effects may be different with lower and higher compositions of the organic solvents as in the case of alcohols.72,97

An adequate organic solvent for this type of studies is ethylene glycol, since it has resemblance with water in certain characteristics. The molecule is small and can form hydrogen bond networks. It also possesses a high cohesive energy and a fairly high dielectric constant. Jha et al.154 have studied the thermodynamics of micellization of Triton X-100 in water-ethylene glycol mixtures and they found that the ethylene glycol-hydrocarbon interactions are more favourable than water-hydrocarbon interactions. Similarly, Palepu and coworkers155 reported the thermodynamic properties of micellization of sodium dodecylsulfate (SDS) in water-ethylene glycol mixed medium whereas Ruiz156
reported the thermodynamics of micellization of tetradecyltrimethylammonium bromide in water–ethylene glycol mixed medium. Recently, Seguin et al. investigated the effects of surfactant head groups on aggregation in water–ethylene glycol and water–1,3-propylene glycol mixtures as well as in pure glycol solutions. The authors have pointed out the possibility of controlling the surfactant aggregation by tuning bulk phase properties. However, it is still not exactly clear which property of a solvent controls the micellization process. Moreover, quantifying solvophobicity and solvophilicity is still an unsolved problem. Studying aggregation behaviour of surfactants in different solvents of varying property therefore provides vital information of fundamental and practical importance. Continued studies on the micellization behaviour of surfactants in various mixed media indicate the importance and relevance of such studies.

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”. They show lower CMC values, better wetting properties, high solubilization capacity and are more effective in reducing the surface tension of water. Geminis have already been utilized in many fields as in skin care, antibacterial regimen, high porosity materials, analytical separations, and solubilization processes. Survey of available literature reveals that only a few attempts have been made to study the micellization phenomenon of gemini surfactants in water–organic mixed solvent systems.
In particular, the choice of cationic gemini surfactants was made in an effort because of the low toxicity of this type of quaternary ammonium surfactants. Also, they exhibit broad spectrum of antibacterial, antifungal activity. As such, the gemini surfactants have already been shown to have germicidal properties greater than those of traditional monoquatemary surfactants. This fact coupled with the (probable) low toxicity of such compounds, and the observed low critical micelle concentrations, suggest that the gemini surfactants may be an appropriate alternative to traditional quaternary ammonium compounds. The implications of the results obtained of gemini micellization may also be useful in micellar catalysis. The study may give insight about the selection of mixed solvent systems for their use in enhanced oil recovery, pharmaceutical and cosmetic applications, washings, chemical reactions, etc. In addition, it is crucial to have knowledge about the effect of water–organic solvent mixed systems on the aggregation of this special class of surfactants for their improved application in other areas.

In view of the above points, we have undertaken a study on the aggregation behaviour of bis(tetradecyldimethylammonium)alkane dibromide (14-s-14, 2Br\(^-\), s = 5, 6) gemini surfactants in various water–organic solvent mixtures. It can be seen from the literature that the gemini surfactants bearing 14 carbon atoms in the alkyl tail have been studied little compared to the that having 12 and 16 carbon atoms in the alkyl chain. Moreover, to our knowledge, till date, no study has been
done to evaluate the effect of various organic solvents on the micellization and related properties of the studied 14-s-14, 2Br\(^-\) geminis.

As discussed under *types of micelles*, mixed micelles are superior in properties compared to the micelles of individual components due to their attainment of enhanced solution properties upon mixing and hence they are more preferred in industrial formulations. Although a number of papers are available on the mixed micellization of various gemini surfactants with different types of amphiphiles, the effect of organic solvents on their mixing behaviour has not been explored. Moreover, a quantitative interpretation of the mixed micellar behaviour of gemini with conventional surfactants at different temperatures is still lacking. Therefore, we have also studied the mixed micelle formation between bis(alkyldimethylammonium)butane dibromides, referred as m-4-m, 2 Br\(^-\), where \(m = 14, 16\) with their conventional counterparts alkyltrimethylammonium bromides (alkyl = tetradecyl and hexadecyl) in presence and absence of ethylene glycol (EG, at a fixed composition) at different temperatures.

**Layout of the thesis**

This thesis consists of the following three chapters:

Chapter-I: General Introduction.

Chapter-II: Experimental.
Chapter-III: Influence of organic solvents and temperature on the aggregation behaviour of bis(tetradecyldimethylammonium)alkane dibromide gemini surfactants.

Chapter-IV: Conductometric and fluorimetric studies on the mixed micelles of bis(alkyldimethylammonium)butane dibromide, (m−4−m, 2Br⁻; m = 14,16), with alkyltrimethylammonium bromide (C₄TAB) surfactants in the presence and absence of ethylene glycol.

References


