General Introduction
1.1 Surfactants

Surfactants are surface-active molecules consisting of a non-polar hydrophobic portion and a polar hydrophilic portion due to which they possess amphiphilic behavior, viz., hydrophobicity and hydrophilicity towards water medium. The polar hydrophilic part of a surfactant molecule is known as head group and the hydrophobic part consisting of hydrocarbon chain with eight or more carbon atoms is called the tail. Surfactants are known to exhibit amphiphilic character in solvents other than water also. Hence, in general, solvophobicity and solvophilicity terms are used to represent the dual characters of surfactants.

1.1.1 Classification

Surfactants can be broadly classified as biosurfactants and synthetic surfactants. Naturally occurring surfactants are called biosurfactants which mostly occur in biological systems. Phospholipids, fatty acids and bile salts are some of the examples of naturally occurring surfactants. Surfactants used for domestic and industrial purposes are mostly synthetic surfactants. Soaps and 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 have the general formula $\text{RA}\overline{\text{M}}^+$, where $\text{R}$ represents the solvophobic chain with $\text{A}^-$ head group and $\text{M}^+$ is the counter ion. These surfactants when dissolved in polar solvents dissociate to give negatively charged monomeric species and the corresponding counter ion and on micellization form anionic micelles. Examples of some of the widely used anionic surfactants are
\( \text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}^+ \) (sodium dodecyl sulfate) and \( \text{RC}_6\text{H}_4\text{SO}_3\text{Na}^+ \) (sodium alkyl benzene sulfonate).

Cationic surfactants carry a positive charge on the head group. In polar solvents these surfactants dissociate to give positively charged surfactant moiety and negatively charged counter ions. These surfactants have the general formula \( RX^+Y^- \). Examples of cationic surfactants are \( \text{CH}_3(\text{CH}_2)_{13}\text{N}^+(\text{CH}_3)_3\text{Br}^+ \) (hexadecyl trimethylammonium bromide) and \( \text{C}_{16}\text{H}_{33}\text{C}_2\text{H}_4\text{N}^+\text{Cl}^- \) (cetyl pyridinium chloride).

Nonionic surfactants do not carry any electrical charge and their aggregates do not have surface charge. Some of the examples of nonionic surfactants are polyoxyethylene (23) dodecanol [brij 35], polyoxyethylene (9-10) octyl phenol [Triton X–100] and polyoxyethylene (20) sorbitan monooleate [Tween 80].

Zwitterionic surfactants possess both anionic and cationic groups on the hydrophobic moiety and depending on the pH of the solution these surfactants can behave as either anionic, cationic or neutral species. The more commonly used zwitterionic surfactants include N-alkyl and C-alkyl betaines, phosphatidyl amino alcohols and acids.

Surfactant molecules containing two hydrophobic tails attached to one head group are also known. Sodium dioctylsulfosuccinate (anionic; commonly known as Aerosol-OT or simply AOT) and dioctadecyldimethylammonium chloride (cationic) are examples of such surfactants. Triple-chained ionic surfactants are also known.\(^2\)
Surfactant molecules containing two head groups and two hydrocarbon chains have also been synthesized. Such surfactants are called gemini (or dimeric) surfactants if the spacer is between the two head groups or bolaforms if the spacer is between the hydrocarbon chain. The length of the spacer can be varied by varying the number of carbon atoms. Efforts are being made to synthesize newer surfactants with special properties, for e.g., photo-sensitive surfactants.

1.1.2 Adsorption and aggregation

Due to their amphiphilic character, surfactants exhibit two very important properties. These are (i) surface activity or adsorption at an interface and (ii) self-organization or aggregation. Due to surface activity, surfactants can lower the surface tension of a solution and form monolayers, films and multilayers. Self-organization or aggregation of surfactants is responsible for the formation of aggregates like micelles, vesicles and membranes. The importance and applications of surfactants in various fields are mainly because of their adsorption and micellization abilities.

1.2 Thermodynamics of adsorption: Gibbs adsorption isotherm

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

\[
\Delta G_\sigma = \gamma \Delta \sigma + \sum_i \mu_i \Delta n_{i\sigma}
\]

(1.1)

where \( \gamma \) is the surface tension, \( \Delta \sigma \) is the change in the area of the surface, \( \mu_i \) is the chemical potential of the \( i^{th} \) component and \( \Delta n_{i\sigma} \) is the change in the amount of the \( i^{th} \) component at the interface. In the light of the thermodynamic principles and by
using the same approach that is used for deriving Gibbs – Duhem equation, we obtain the relation

\[ d\gamma = -\sum_i \Gamma_i \, d\mu_i \]  \hspace{1cm} (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 \( i^{th} \) component. \( \Gamma_i \) is the surface excess of the \( i^{th} \) component and is defined as

\[ \Gamma_i = \frac{n_{i\sigma}}{\sigma} \]  \hspace{1cm} (1.3)

\( n_{i\sigma} \) 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

\[ d\gamma = -\Gamma_1 \, d\mu_1 - \Gamma_2 \, d\mu_2 \]  \hspace{1cm} (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

\[ d\gamma = -\Gamma_2 \, d\mu_2 = -RT \, \Gamma_2 \, d\ln a_2 \]  \hspace{1cm} (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 \( c_2 \). For a surfactant solution, we can now write the Gibbs adsorption isotherm as

\[ \Gamma = -\left(\frac{1}{RT}\right) \left(\frac{d\gamma}{d\ln c}\right) \]  \hspace{1cm} (1.6)

where \( c \) and \( \Gamma \) are the concentration and surface excess of the surfactant, respectively. Since \( \Gamma \) is positive for surfactants, \( d\gamma/d\ln c \) 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. Due to the ability of surfactants to lower interfacial tension, they are used as emulsifiers, foaming agents, etc.

1.3 Gibbs adsorption isotherm for ionic surfactants

Since we have studied in this thesis cationic surfactants in the presence of electrolytes, the Gibbs adsorption isotherm given by Eq. (1.2) has been looked into in more detail in the light of the treatment reported by Prosser and Franses. We consider here an cationic surfactant RM in aqueous medium in the presence of an added electrolyte XM. The dissociations of RM and XM in the bulk solution are given by

\[
\text{RM} \rightarrow n_+ \text{R}^{z+} + n_- \text{M}^{z-} \quad (1.7) \\
\text{XM} \rightarrow n_{+e} \text{X}^{s+} + n_{-e} \text{M}^{s-} \quad (1.8)
\]

\(\text{R}^{z+}\) is the surfactant cation having charge \(z_+\) and \(\text{M}^{z-}\) is the counter ion having charge \(z_-\). \(\text{X}^{s+}\) is an indifferent non-adsorbing co-ion and \(\text{M}^{s-}\) is the counter ion contributed by the added electrolyte, which is considered to be the same as the surfactant counter ion. \(n_+\) and \(n_-\) are the number of moles of surfactant ion and counter ion produced by the dissociation of one mole of surfactant, respectively. Similarly, \(n_{+e}\) and \(n_{-e}\) are the number of moles of \(\text{X}^{s+}\) and \(\text{M}^{s-}\) produced by the dissociation of one mole of electrolyte, respectively. Since the counter ion is same, \(z_- = s_-\). Let \(c_M\), \(c_R\) and \(c_X\) be the concentrations of the ionic species, \(\text{M}^{z-}, \text{R}^{z+}\) and \(\text{X}^{s+}\) in the solution, respectively. The Gibbs adsorption isotherm
given by Eq. (1.2) can now be written in the expanded form for the solution containing RM and XM as

\[ d\gamma = -RT\left[ \Gamma_M d\ln c_M + \Gamma_R d\ln c_R + \Gamma_X d\ln c_X \right] \quad (1.9) \]

where, \( \Gamma_M, \Gamma_R \) and \( \Gamma_X \) are the surface excess of ionic species, \( M^{z-}, R^{z+} \) and \( X^{s+} \), respectively. If \( c \) and \( c_e \) are the bulk concentrations of surfactant and electrolyte, respectively, then the ion concentrations are related to the known bulk concentrations as

\[ c = \frac{c_R}{n_+}, \quad c_e = \frac{c_X}{n_{+e}} \quad (1.10) \]

If \( \Gamma \) and \( \Gamma_e \) are the surface excess of the surfactant and the electrolyte, then

\[ \Gamma = \frac{\Gamma_R}{n_+}, \quad \Gamma_e = \frac{\Gamma_X}{n_{+e}} \quad (1.11) \]

Electro-neutrality condition gives the following relations:

\[ z_- = \frac{n_+z_+}{n_-}, \quad s_- = z_- = \frac{n_{+e}s_+}{n_{-e}} \quad (1.12) \]

\[ c_M = n_-c + n_{-e}c_e \quad (1.13) \]

\[ z_-c_M = s_+c_X + z_+c_R = s_+n_{+e}c_e + z_+n_+c = n_{-e}z_-c_e + n_-z_-c \quad (1.14) \]

\[ z_-\Gamma_M = z_+\Gamma_R + s_+\Gamma_X \quad (1.15) \]

Substituting Eqs. (1.10) - (1.15) into Eq. (1.9) and by considering the surface excess of co-ion, \( \Gamma_X \), to be zero, we get after rearrangement

\[ d\gamma = -RT\Gamma d\ln [c_R^{n_+}(n_-c + n_{-e}c_e)^{n_-}] \quad (1.16) \]

For a symmetric univalent surfactant and added electrolyte, Eq. (1.16) takes the form

\[ \gamma = -RT\Gamma [d\ln(c + c_e) + d\ln c] \quad (1.17) \]
In the absence of an electrolyte, for surface excess of a symmetric univalent surfactant one gets from Eq. (1.17) an expression of the type

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

(1.18)

Equation (1.16) on differentiation and further rearrangement yields an expression for the surface excess of a surfactant in the presence of a particular concentration of an electrolyte, which is of the form

\[ \Gamma = -\left( \frac{1}{RT} \right) \left( \frac{1}{n_+ + \frac{n^2 c}{n-c + n ec_e}} \right) \left( \frac{dy}{d\ln c} \right) c_e \]  

(1.19)

Thus, from the above expressions the amount of an ionic surfactant adsorbed at the air – water or air – solution interface can be quantitatively estimated. If both the ionic surfactant and the added electrolyte are 1:1 type, then \( n^+ = n^- = n^{-e} = 1 \) and Eq. (1.19) becomes

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

(1.20)

1.4 Micelle formation

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. Hydrophobic interaction is considered to be responsible for micellization of a surfactant. Water molecules become more ordered around the hydrocarbon tail of a surfactant. Transfer of hydrophobic tails of a surfactant from bulk water into micellar phase results in positive entropy change due to disordering of the ordered water molecules around
the hydrocarbon tail. The entropy generated thus in the solvent medium drives the micellization process. Micelles formed in polar solvents are called normal micelles, whereas those formed in non-polar solvents are called reverse micelles.

1.5 Micellization parameters

Micellization of surfactants in solution always begins at a particular critical concentration known as the critical micelle concentration (cmc). When micelle is formed, a sudden change in several physical properties of surfactant solutions takes place enabling us to determine experimentally values of cmc of surfactants. 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 one of the important properties of a surfactant by which its micellization behavior is characterized. Cmc depends on the structure of surfactant and on the concentration of added electrolytes. 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 of ionic and nonionic surfactants with
identical hydrophobic moieties indicating the influence of hydrophilic group on cmc. The lower cmc 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 affects the value of cmc of ionic surfactants. Added electrolytes have significant effect on the cmc of both ionic and nonionic surfactants. The addition of electrolytes also affects other properties of surfactants like cloud point, free energy of micellization, aggregation number, etc. Non-electrolytes like urea, amides, alcohols, etc on addition produce both increase and decrease of cmc of surfactants. The temperature dependence of cmc is quite interesting. Most of the ionic surfactants exhibit at some temperature a minimum in the cmc. This property of ionic surfactants is used in the differential scanning calorimetry technique for studying the micellization behavior of ionic surfactants. With increase in pressure cmc of ionic surfactants in water show a maximum.

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. Aggregation number also shows dependence on the structure of a surfactant and on the amount of added electrolyte. Marked changes in the aggregation number of surfactants indicate about changes in the micellar shape. Unlike cmc, aggregation number has dependence on the surfactant concentration. In a particular surfactant solution micelles of different aggregation number can exist. Such polydispersity is generally ignored for calculation purpose and only monodispersed micelles with
single (average) aggregation number are taken into account. Aggregation number is determined using experimental techniques like quasi-elastic light scattering, small-angle neutron scattering, steady-state fluorescence quenching and time-resolved fluorescence quenching.\textsuperscript{22-24, 28, 29, 52, 56, 57}

Counter ion binding constant ($\beta$) is another important characteristic of ionic micelles. Counter ions control, besides cmc and aggregation number of ionic surfactants, also the reactions\textsuperscript{58} 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 lower value than in water.

Thermodynamic functions such as Gibbs function, enthalpy and entropy of micellization and surface potential of ionic surfactants are other related micellization parameters. 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. Some other parameters/properties of surfactants that are related to their micellization are Kraft temperature, cloud point and solubilization.

1.6 Structure and shape of ionic micelles

Micelles have regular structures and shapes. A general structure of a regular ionic micelle formed in polar solvents\textsuperscript{59} is shown in Fig. 1.1. An ionic micelle consists of a liquid core or interior, which is oil like, formed by the associated hydrocarbon chains. 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. The shear layer lies between the Stern and the diffuse layers.
Appreciable amount of water has been reported\textsuperscript{60,61} to penetrate into the liquid-like
hydrocarbon core.

Since micelles are in dynamic equilibrium with the surfactant monomers,
considering them to have rigid structures with precise shapes may be unrealistic.
Small-angle neutron scattering experiments on micellar solutions,\textsuperscript{23,52,56,62,63}
dynamic light scattering experiments and phase diagram studies support the concept
of micelles having regular shapes.\textsuperscript{22-24,52,64,65} It is assumed that micelles at
concentrations near to the cmc 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.
The other proposed structures of micelles include the rod-like,\textsuperscript{66} the lamellar
model\textsuperscript{67} and the disk or cylindrical model.\textsuperscript{68} Added electrolyte has great influence
on the shape of ionic micelles. As the counter ion concentration is increased, the
shape of ionic micelles changes in the sequence spherical – cylindrical – hexagonal
– lamellar.\textsuperscript{22,23,65,69-71} Some of the shapes of micelles are shown in Fig. 1.2.
Geometrical parameters like surface area of the head group, alkyl chain length,
molecular volume of the hydrocarbon chain, etc. control the shapes adopted by
micelles.\textsuperscript{26}

1.7 Thermodynamics of micelle formation

Two approaches are used to understand the thermodynamics of the
micellization process, which are Phase – Separation and Mass – Action models. In
the Phase – Separation model the micelles are considered to form a separate phase
at the cmc in equilibrium with the solution phase, while in the Mass – Action
model micelles and unassociated monomers are considered to be in association-
dissociation equilibrium. The two models merge asymptotically with increasing
aggregation number. Besides these two approaches thermodynamics of small
systems developed by Hill\textsuperscript{72} has also been applied to the aggregation of solutes. The
phase – separation and the mass – action models are briefly discussed below.

1.7.1 Phase – Separation model

In this approach the micelle is treated as a separate phase. Appropriate
standard states are to be defined first in order to calculate the thermodynamic
parameters of micellization. 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.\textsuperscript{73, 74}

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 cmc

$$\mu_s = \mu_m$$

(1.21)
For a non-ionized surfactant

\[ \mu_s = \mu_s^0 + RT \ln a_s \]  

(1.22)

\( \mu_s^0 \) corresponds to the chemical potential at the standard state. It is assumed that the concentration of free monomers is low and this permits one to replace the activity, \( a_s \), of surfactant monomers by its mole fraction, \( X_s \). The above Eq. (1.22) is therefore written as

\[ \mu_s = \mu_s^0 + RT \ln X_s \]  

(1.23)

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

\[ \mu_m = \mu_m^0 \]  

(1.24)

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

\[ \Delta G_{mic}^0 = \mu_m^0 - \mu_s^0 = \mu_m - \mu_s + RT \ln X_s = RT \ln X_s \]  

(1.25)

Assuming that the concentration of free surfactant in the presence of micelle is constant and equal to the critical micelle concentration, we get \( X_s = X_{cmc} \). Eq. (1.25) therefore becomes

\[ \Delta G_{mic}^0 = RT \ln X_{cmc} \]  

(1.26)

In the case of ionic surfactants, \( \Delta G_{mic}^0 \) 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 consists of \( n \) moles of surfactant monomer and \( m \) moles of counter ion, \( \beta = m/n \). \( n \) is 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 equation (1.26) therefore modifies to

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

(1.27)

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. (1.27) becomes

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

(1.28)

1.7.2 Mass – Action model

According to this model in the case of 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

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

(1.29)

In the above equilibrium $R^+$, $M^-$ 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

$$
K = \frac{a_A}{a_R a_M}
$$

(1.30)

$a_A$, $a_R$ 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

$$
\Delta G^0_{\text{mic}} = -\frac{RT}{n} \ln K
$$

(1.31)
Substituting the value of $K$ from Eq. (1.30), we get

$$\frac{\Delta G_{\text{mic}}^0}{RT} = -\left(\frac{1}{n}\right)\ln a_A + \ln a_R + \left(\frac{m}{n}\right)\ln a_M$$ \hspace{1cm} (1.32)

Eq. (1.32) can be rearranged to the form

$$\ln a_R = \left[\frac{\Delta G_{\text{mic}}^0}{RT} + \left(\frac{1}{n}\right)\ln a_A\right] - \left(\frac{m}{n}\right)\ln a_M$$ \hspace{1cm} (1.33)

Near the cmc, which generally falls in the low concentration region for most of the ionic surfactants, activity terms can be approximated to concentration terms and Eq. (1.33) becomes

$$\ln c_R = \left[\frac{\Delta G_{\text{mic}}^0}{RT} + \left(\frac{1}{n}\right)\ln c_A\right] - \left(\frac{m}{n}\right)\ln c_M$$ \hspace{1cm} (1.34)

Just above the cmc, we can approximate

$$c_R \approx c_0 \quad \text{and} \quad \frac{\Delta G_{\text{mic}}^0}{RT} + \left(\frac{1}{n}\right)\ln c_A \approx \frac{\Delta G_{\text{mic}}^0}{RT}$$ \hspace{1cm} (1.35)

c_0 denotes cmc. Eq. (1.34) now becomes

$$\ln c_0 = \frac{\Delta G_{\text{mic}}^0}{RT} - \beta \ln c_M$$ \hspace{1cm} (1.36)

In mole fraction units Eq. (1.36) can be written as

$$\ln X_{\text{cmc}} = A - \beta \ln X_M$$ \hspace{1cm} (1.37)

where $\Delta G_{\text{mic}}^0/RT$ is represented by $A$. Eq. (1.37) is similar to Eq. (1.28). Eqs. (1.27), (1.28), (1.36) and (1.37) are the different forms of the Corrin – Harkins equation.75
1.8 Scope of the work

Electrolytes and non-electrolytes on addition alter the micellization characteristics of surfactants and hence affect their performance. In almost all formulations containing surfactants different additives are used so that these formulations acquire the required properties. Therefore, it is of practical/industrial importance to study the effect of additives on the micellization parameters of surfactants.

Generally, the effect of added electrolyte on micellization parameters is entirely attributed to the counterions. However, both counterion and coion of an added electrolyte may have influence on the adsorption and aggregation properties of an ionic surfactant.

Added counterions normally increase the surface excess, decrease the critical micelle concentration (cmc) and increase the aggregation number of ionic surfactants. Counterions also decrease the surface potential of ionic micelle and induce shape change of micelles. In some ionic surfactants, added counterions on exceeding a particular concentration alter even the value of counterion binding constant.

Scattered works indicate that co-ions can also affect the behaviour and performance of ionic surfactants. Muller and Birkhahn were the first to report on the effect of coions on the cmc. They reported that the cmc values of \( \text{CF}_3(\text{CH}_2)_8\text{COONa} \) and \( \text{CF}_3(\text{CH}_2)_{10}\text{COONa} \) in aqueous NaOH and NaCl solutions were different. Ikeda et al. reported that the aggregation number (or molecular weight) of sodium dodecylsulfate micelles in aqueous solutions of sodium salts changed in the order \( \text{NaSCN} < \text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI} \). The study made by
Ranganathan et al.\textsuperscript{92} on the dynamics of incorporation of N-alkylpyridinium ions into cetyltrimethylammonium chloride and acetate surfactants is indicative of coion–micelle interactions. The effect of acetate and propionate coions on the cmc of SDS observed by us from conductance study\textsuperscript{77} has, however, not been detected by tensiometry.\textsuperscript{93} Kabir-ud-Din et al.\textsuperscript{94} had investigated the influence of LiCl, NaCl and KCl on the hexanol concentration required to produce the relative viscosity maximum in the 0.2 mol dm\textsuperscript{-3} CPC solution + hexanol system and reported that the co-ion effect is not significant.

In the light of the above reports, it is obvious that coions can produce perceivable changes in the values of micellization parameters and can also affect the solubilization process of surfactant systems. In order to obtain a clear understanding of the role of coions in the adsorption and micellization behaviours of ionic surfactants, it is necessary to study and document the adsorption and micellization characteristics of ionic surfactants in the presence of electrolytes containing different co-ions. Furthermore, the effect of mixed counter ions on the micellization characteristics of ionic surfactants has not been investigated in detail.

Therefore, the objective of the work is to investigate the effect of coions as well as counterions on the adsorption and aggregation behaviours of ionic surfactants. In this thesis, we have chosen cetylpyridinium chloride (CPC) as the surfactant (a cationic surfactant) for investigation. The adsorption and aggregation behaviours of CPC have been investigated in the presence of different types of electrolytes with varying coions and counterions. The effect of electrolyte has been investigated by changing the solvent also.
In chapter 3, surface tension and conductance studies of CPC in aqueous medium in the presence of LiCl, NaCl and KCl were carried out. In chapter 4, similar studies of CPC were made in aqueous medium in the presence of sodium salicylate and sodium benzoate. Sodium salicylate and sodium benzoate are electrolytes having hydrotropic property. In chapter 5, we carried out surface tension and conductance studies of CPC in aqueous sodium bromide and tetrabutylammonium bromide media.

Solvents play a decisive role in controlling the adsorption and micellization characteristics of surfactants. Mixing of solvents changes solvent property, particularly polarity, and we get important results of fundamental and practical importance by carrying out adsorption and aggregation studies of surfactants in mixed solvents. Due to this reason, surfactant behavior is being studied in binary mixtures of solvents with a renewed interest in the last four years. In view of this, in chapter 6 surface tension and conductance studies of CPC were made in water + glycerol medium in the absence and presence of NaCl.
Figure 1.1 - A schematic representation of a spherical ionic micelle showing bound counter ions and the electrical double layer.

Figure 1.2 - Schematic representation of different shapes of micelles
1.11 References


