Chapter - I

General Introduction
Supramolecular aggregates and assemblies such as association colloids, vesicles, biological membranes, monolayers, proteins, DNA, polyelectrolytes, and ion-exchange resins all share an important structural feature, an interfacial region of moderate polarity juxtaposed to a highly polar aqueous region.\textsuperscript{1-8} Association colloids are dynamic aggregates of amphiphilic molecules which also have a substantial nonpolar region adjacent to the interfacial region composed of aggregated hydrocarbon chains.

Nature has the ability to manipulate and control the structures of aggregates formed by simple amphiphilic molecules – surfactant monomers being one of them. The demand for materials with improved and novel properties has now changed the emphasis in surfactant research to study new phenomenon in fascinating world of surfactants with highly controlled molecular architectures.\textsuperscript{9-11}

An amphiphilic substance, when present at low concentration in a system, has the property of getting adsorbed onto the surfaces or interfaces of systems and of altering the surface free energies of those systems to a marked degree.\textsuperscript{12,13} Due to this property they are often called surface active agents or surfactants.\textsuperscript{14}

Surfactants have a polar hydrophilic head group at one end and a nonpolar hydrophobic moiety connected to the head group on the other end. They are mostly derived from fatty acids, fatty alcohols, alkylphenols, alkylamines, and mercaptans. Typical examples are soaps or phospholipids which form membranes.
The hydrophobic part is usually a long hydrocarbon chain. It can be of different lengths, can contain unsaturated portions or aromatic moieties and can be branched or consist of two or more chains. The polar or the ionic head group may have distinctive variations. Many surfactants, such as the physiologically important bile salts, have rigid structures as opposed to the flexible chains of soaps and detergents.

Surfactant, in general, can be ionic or nonionic depending on whether its head group ionizes in water or not. The ionic surfactants are further classified as cationic or anionic by the charge of the head group. Cetyltrimethylammonium bromide (CTAB) is an example of cationic surfactant in which CTAB monomer dissociates as CTA⁺ and Br⁻ ions in aqueous medium. Similarly, sodium dodecyl sulfate (SDS), which consists of negatively charged DS⁻ and Na⁺ ions, is an example of anionic surfactant.

An exhaustive list of both synthetic and naturally occurring surfactants is available. Their preparation and properties, in general, have been given in the monograph of Fendler and Fendler.\(^{15}\)

When surfactant molecules are dissolved in water, they segregate their hydrophobic portion from water, by associating into a variety of aggregate structures, called micelles.\(^{2,4,16-19}\) The coexistence of two opposite types of behavior (hydrophilic and hydrophobic) inside the same molecule is the origin of local constraints which lead to spontaneous aggregation. These structures, at thermodynamic equilibrium, give surprising macroscopic properties to the solution.
Micellar aggregation can be demonstrated by measuring solution properties, such as surface tension, osmotic pressure, viscosity, electrical conductivity, and density, against surfactant concentration. As the surfactant concentration is increased gradually, these properties abruptly change over a narrow range of concentration. This suggests that there is a concentration below which aggregation is absent and above which aggregates would form and that these aggregates affect the thermodynamic properties of the solution. This threshold concentration of surfactant is called the critical micellar concentration (cmc).

The magnitude of this concentration range depends on the physical property being measured. The discontinuity in the property of the solution can be used to identify the cmc. Some other techniques which have been developed to determine the cmc include dye solubilization, water solubilization, $^1$H NMR, light scattering, fluorimetry, etc. The different experimental methods available for determining the cmc are summarized by Shinoda et al., and Elworthy et al. and are discussed by Mukerjee and Mysels. The latter authors have also compiled cmc values and have evaluated different methods used for their determination.

Micelles are not frozen objects. They are noncovalently bonded macromolecular aggregates that are of highly dynamic character. The alkyl chains constituting the micellar core are in constant motion and the water molecules, the counterions and the surfactant ions are continually and reversibly exchanging between micelle bound and free states. Kinetic studies indicate that the lifetime of a monomer in the micelle is about 0.01–1 ms.
The effective attractive tail-tail interaction, due to the hydrophobic interaction, lowers the free energy of the system\(^2\) \text{(i.e., surfactant + water). Transfer of monomer into micelle means that the structuring of water around the hydrocarbon part of the monomer is lost, therefore, an ordered state has become a disordered one with regard to the water, implying a positive entropy change and a decrease in free energy. These factors favor micelle formation. On the other hand, the electrostatic and the steric repulsive interactions between the polar head groups will act to increase the free energy of the system. Also, formation of ordered aggregates from disordered dispersed monomers in solution will decrease the entropy of the system. These two factors will oppose the aggregation. The overall decrease in free energy due to loss of hydrocarbon/water interfacial energy and water structure outweighs the free energy increase due to electrical work and translational freedom losses, giving a remarkable tendency to micellize.

For nonionic surfactants, no electrical force is expected to oppose micellization, so they form micelles at lower concentrations than the ionic ones.

Types of Micelles

\textit{Normal Micelles}

The structure of a normal micelle just above the cmc can be considered as roughly spherical (Fig. 1.1).\(^{28,29,32}\) When the hydrophobic portion of the surfactant is a hydrocarbon chain, the micelle will consist
Fig. 1.1. A two-dimensional schematic representation of the regions of a spherical ionic micelle. The counterions (X), the head groups (Θ), and the hydrocarbon chains (\(^{\wedge}\wedge\)) are schematically indicated to denote their relative locations but not their number, distribution, or configuration.
of a liquid like hydrocarbon core. The radius of this core is roughly equal to the length of fully extended hydrocarbon chain (\(\sim 12-30 \text{ Å}\)). The polar head groups and bound water are regularly arranged at the micellar surface which is rough.\textsuperscript{33} Menger has proposed that water can penetrate inside the micelle up to a certain level,\textsuperscript{34,35} the idea gets support from fluorescence and \(^1\text{H} \text{NMR} \text{ measurements}. \text{Partial molar volume determinations indicate that the alkyl chains in the core are more expanded than those in the normal liquid state.}\textsuperscript{36}

The nonionic micelles arrest water molecules at the palisade layer by hydrogen bonding of water with the polyethylene oxide groups.\textsuperscript{37} Water may remain trapped in this region.

In ionic micelles, the surface potentials are high\textsuperscript{33,38} and a significant fraction of the counterions (60–90 \%)\textsuperscript{3} are located in a compact region, known as 'Stern layer',\textsuperscript{33} which extends from the core to within a few angstroms of the shear surface of the micelle. The core and the Stern layer form the 'kinetic micelle'. Most of the remaining counterions are, however, located outside the shear surface in the region called 'Gouy-Chapman electrical double-layer'. The charge of the kinetic micelle is neutralized by these counterions.

Counterions are "bound" primarily by the strong electrical field created by the head groups but also by specific interactions that depend upon head group and counterion type.\textsuperscript{3,32,39} A two-site model has been successfully applied to the distributions of counterions; \textit{i.e.}, they are
assumed to be either "bound" to the micellar pseudophase or "free" in the aqueous phase.\textsuperscript{8,16,40} The head group and counterion concentrations in the interfacial region of an ionic micelle are on the order of 3–5 M, which gives the micellar surface some of the properties of concentrated salt solutions.\textsuperscript{8,38,41} Although the solution as a whole is electrically neutral, both the micellar and aqueous pseudophases carry a net charge because thermal forces distribute a fraction of the counterions radially into the aqueous phase.\textsuperscript{8,16}

**Reverse Micelles**

Surfactants in nonpolar solvents in presence of traces of water associate to form the so-called reverse, inverted or reverted micelles. The structure of micelle is similar to that of normal micelle but inversed, \textit{i.e.}, the polar head groups of the monomers being present in the centre and the hydrocarbon chains extending outwards into the solvent (Fig. 1.2).\textsuperscript{42,43} Water forms a pool in the interior of the micellar aggregate. The size and properties of reverse micelles vary with the amount of water present.\textsuperscript{44,45}

Water in reverse micelles is expected to behave very differently from ordinary water because of extensive binding and orientation effects induced by the polar heads forming the water core.\textsuperscript{46}

**Mixed Micelles**

The formation of micelles from more than one surfactant gives rise to mixed micelles. Clint\textsuperscript{47} developed an analytical description which contained both micelle composition and monomer concentration above the
Fig. 1.2. Schematic structure of a spherical reverse micelle.
mixed cmc for mixtures of nonionic surfactants. Clint's treatment assumed ideal mixing in the micelle. Furthermore, the expressions of Lange and Beck\textsuperscript{48} and Clint\textsuperscript{47} for the cmc values of mixtures of nonionic surfactants have been experimentally verified for cases where ideal mixing might be expected. The properties of the mixtures of ionic and nonionic surfactants\textsuperscript{49-51} have been interpreted with the aid of mixed micelle formation. It was pointed out that the cmc of the mixed surfactants was lower than either of the single surfactants\textsuperscript{47,48}.

Clint's theory of ideal mixing can hardly account for the characteristics of mixed systems of dissimilar structural features. Rubingh\textsuperscript{52} formulated a theoretical treatment to relate the monomer concentration to the micellar composition. Although found to be reasonably satisfactory in many cases\textsuperscript{53,54} the theory was criticized on thermodynamic grounds. Recently, Sarmoria \textit{et al.}\textsuperscript{55} and Puvvada \textit{et al.}\textsuperscript{56-58} have developed a molecular thermodynamic model for mixed surfactant systems. The description of mixed surfactant solutions available in literature are mostly based on Rubingh's approach mainly because it includes a specific interaction parameter $\beta$ giving a measure of the interaction of the surfactant species in solution. However, Haque \textit{et al.}\textsuperscript{59} have observed anomalies in Rubingh's approach.

Mixed micelles may also form when low molecular weight solutes are solubilized by micelles of surfactants containing a relatively larger nonpolar side chain. The solubilized substances, also called as the
penetrating additives,\textsuperscript{60} may be located in both the hydrocarbon core\textsuperscript{61} and in the hydrophilic mantle.\textsuperscript{62-64}

The occurrence of mixed surfactants and hence mixed micelles are common in industrial, pharmaceutical and biological fields; physicochemically, they work better than pure surfactants in solution.

**Factors Affecting Critical Micellar Concentration**

The reason for micelle formation, in general terms, is the tendency of the hydrocarbon part of the monomer to associate with itself rather than to remain in close proximity with water. Micelle formation is thus an outstanding example of what is known as 'hydrophobic bonding'.

The cmc and solution properties depend upon the chemical structure of surfactants as well as physicochemical conditions such as the concentration of added salts,\textsuperscript{14,33} solvent polarity, temperature, pH, and pressure.\textsuperscript{19}

The polarity of the medium favors surfactant association. Nonpolar medium offers environment similar to the surfactant tail so that their tendency of self-association is reduced. In a good nonpolar medium, viz., cyclohexane, carbon tetrachloride, etc., formation of normal micelle may be totally absent; instead, a reverse orientation (reverse micelle) may occur.

Generally, the cmc decreases as the chain length increases. For the same head group, compounds containing longer hydrocarbon chains form
micelles at lower concentrations than those containing short chains. The position of head group in hydrocarbon chain also affects the cmc. The closer the head group to the centre of the chain, the higher the cmc; due to the two branches of the chain partially shielding one another. The presence of double bond in the chain also causes an increase in cmc.

The effect of temperature on cmc is essentially guided by the way temperature affects the solubility and other behaviors of surfactants in solution. In general, for ionic surfactants the cmc first decreases in the lower range of temperature, at higher temperature range, it increases.\textsuperscript{65} Decrease in cmc at low temperature is probably due to desolvation of parts of monomer which make it more hydrophobic. cmc increase is due to thermal agitation of molecules resulting in a decreased adhesion between monomers. For nonionic surfactants the cmc decreases with increasing temperature.\textsuperscript{66,67} The micelle size of the ionic surfactants decreases\textsuperscript{68} and that of nonionic surfactants increases\textsuperscript{69} with temperature.

cmc has been found to first increase upto a pressure of 1000 atm and decrease with further increase of pressure.\textsuperscript{70-72} This is due to water structure destruction by the applied thrust to assist wider distribution of the surfactant molecules in solution to oppose their tendency of association. The decrease in cmc may be due to an increase in the dielectric constant of water, making less electrical work necessary to bring a monomer into a micelle.

Addition of polar and nonpolar substances to surfactant solutions may also alter the cmc, aggregation number (n), size and shape of
micelles. In ionic surfactants the cmc decreases with the addition of salts\textsuperscript{73-77} because the screening action of the simple electrolytes lowers the repulsive forces between the polar head groups. The addition of salts in nonionic surfactants have been found to decrease\textsuperscript{78-81} and then increase\textsuperscript{80} the cmc. This may be due to a reduction in the hydration of the monomers, which increases their hydrophobicity and, consequently, their tendency to micellize. The micelle size increases\textsuperscript{78} with increased salt concentration. The effective charge on the micelles, $\alpha$ (the number of charges per micelle), increases with salt concentration but the actual degree of dissociation, $\alpha/n$, remains roughly constant.

Non electrolytes may both increase and decrease the cmc of surfactants,\textsuperscript{28,82} like urea and its derivatives increase the cmc of both ionic and nonionic surfactants.\textsuperscript{60,83,84} Urea is generally believed to break the water structure\textsuperscript{60,83} and to decrease the structure around the hydrocarbon chains, hence reducing the driving forces for micellization. This effect is generally greater for cationic micelles than for anionic micelles. Addition of acetamide and formamide decrease the cmc of surfactants.\textsuperscript{85}

Low concentrations of added alcohols reduce the cmc, but high concentrations tend to increase it for both ionic\textsuperscript{60,86} and nonionic surfactants.\textsuperscript{87} It has been found that micelles disappear by the addition of some organic solvents to aqueous solution of surfactants.\textsuperscript{88,89}

cmc of surfactants were found to be lower in $\text{D}_2\text{O}$ than in $\text{H}_2\text{O}$\textsuperscript{60,90} because hydrophobic bonds may be stronger in $\text{D}_2\text{O}$ than in $\text{H}_2\text{O}$.\textsuperscript{91}
Aggregation Number and Minimum Micellar Size

The number of surfactant molecules which aggregate to form a micelle is called aggregation number of that surfactant. The methods of light scattering and fluorescence quenching are conveniently used to estimate the aggregation number.\cite{92,93} Normally, the aggregation number falls in the range of 20–200; the bile salt micelles can have lower aggregation number\cite{94} of 4–10. The aggregation number is affected by different factors such as the nature of the surfactant, temperature,\cite{2,7,95,96} type and concentration of added electrolyte,\cite{2,97,98} organic additives,\cite{14,100,102} etc.

A micellar aggregate tends to form a close packed core consisting of hydrocarbon tails, each having a well defined steric volume, \(v\). The head groups distribute themselves uniformly on the surface of the core and try to maintain an optimum surface area per head group, \(a_o\).

If \(n\) be the minimum aggregation number, volume conservation relation and surface area conservation relation are, respectively,

\[
 n \, v = \frac{4}{3} \pi \, r^3 \quad \text{ (1.1)}
\]

and

\[
 n \, a_o = 4 \pi r^2 \quad \text{ (1.2)}
\]

where \(r\) is radius of the hydrocarbon core. Eq. (1.1) states that volume of the hydrocarbon core is equal to the sum of the steric volumes of each hydrocarbon tail in the core. Eq. (1.2) asserts that the surface area per head group is equal to the optimum value \(a_o\).
For a spherical micelle it is reasonable to assume that the radius \( r \) of the micelle will be equal to the length \( l_e \) of the surfactant molecule. Thus the values of \( a_o \) and \( n \) can be calculated in terms of \( v \) and \( l_e \). It can be shown that
\[
a_o = 3v/r \sim 3v/l_e
\]
and
\[
n = 4\pi r^3/3v \sim 4\pi/l_e^3/3v
\]
(1.3)
(1.4)

\( v \) and \( l_e \) of the hydrocarbon tail can be calculated using Tanford's formula
\[
v = (27.4 + 26.9n_c) \text{ Å}^3
\]
(1.5)
and
\[
l_e = (1.5 + 1.265n_c) \text{ Å}
\]
(1.6)

where \( n_c \) is the number of carbon atoms per chain.

For example, \( n_c \) is 12 for SDS and 16 for CTAB and this gives \( v = 350.2 \text{ Å}^3 \) and \( 457.8 \text{ Å}^3 \) for SDS and CTAB, respectively. \( l_e \) for SDS and CTAB comes out to be 16.7 Å and 21.74 Å, respectively.

Eqs. (1.3) and (1.4) along with eqs. (1.5) and (1.6) suggest that for \( n_c = 12, n \sim 56 \) and for \( n_c = 16, n \sim 94 \). These values are consistent with the experimental results as has been reported for SDS and CTAB.\(^{15}\)

**Structures of Micelles**

Micelles, unlike solid particles or rigid macromolecules such as
DNA, are soft and flexible, *i.e.*, fluid like. This is because the forces that hold surfactant molecules together in micelles are not due to covalent or ionic bonds but arise from the weaker van der Waals, hydrophobic, hydrogen bonding and screened-coulombic interactions. Thus, if the solution conditions such as temperature, electrolyte concentration, or the pH of the micellar solution are changed, it would affect both intra- as well as inter-aggregate interactions, thereby modifying the shape and size of the structures themselves.\textsuperscript{103-110}

The shape and size of these micellar aggregates can, in principle, be determined by various methods such as viscosity,\textsuperscript{111-116} light scattering,\textsuperscript{69,97,117,118} diffusion sedimentation velocity, sedimentation equilibrium,\textsuperscript{119,120} ultrasonic absorption,\textsuperscript{121,122} time-resolved fluorescence,\textsuperscript{78,123} small-angle neutron scattering (SANS),\textsuperscript{124,125} etc. Transition of spherical to larger micelles for ionic surfactants occurs upon a reduction of interhead group repulsions.\textsuperscript{126,127} It may be caused by salt\textsuperscript{128} or surfactant\textsuperscript{129,130} additions or solute solubilization.\textsuperscript{60,61}

Packing considerations constitute a factor which involves the nature of the head and tail groups of the surfactant. A critical ratio ($R_p$) has been devised by Ninham and co-workers,\textsuperscript{131,132} defined as

$$R_p = \nu/a_o l_c$$

(1.7)

The $R_p$ depends on chemical structure of the surfactant monomer ($l_c$ and $\nu$) and on surface repulsion between head groups. The desired
curvature and thus type of aggregate may be obtained upon a correct choice of the surfactant molecule and solvent conditions (type of solvent, ionic strength, etc.) using $R_p$ value as a guide (Fig. 1.3). However, the ratio has to be used with caution as it accounts only for geometrical considerations. In three and four component systems, by using this $R_p$ value, Fang \textsuperscript{133} explained a series of phase transitions (starting with normal micelles and ending with reverse micelles).

\textit{Spherical Micelles}

Spherical micelles are formed when the surfactant molecules has comparatively large head group area and a small volume. Eqs. (1.1) and (1.2) give $v/a_o r = 1/3$. For spherical micelles $r \leq l_c$ and, therefore, $v/a_o l_c \leq 1/3$. Thus, the surfactant molecules with packing parameter, $R_p \leq 1/3$ form spherical micelles. The size of the spherical micelle is not very sensitive to the surfactant concentration and the micelles are fairly monodisperse. The examples of such surfactants which form nearly spherical micelles are SDS\textsuperscript{60,134} and dodecyltrimethylammonium bromide (DTAB).\textsuperscript{135,136}

\textit{Cylindrical Micelles}

Non spherical micelles, such as cylindrical or ellipsoidal, are formed for the value of the packing parameter $1/3 \leq R_p \leq 1/2$. The surfactant molecules with small head group or large volume will form non spherical micelles. For example, CTAB forms ellipsoidal micelles (Fig. 1.4).\textsuperscript{137,138} Spherical micelles can be changed to rodlike or cylindrical micelles, vesicles or bilayers by increasing the salt concentration or lowering the
Fig. 1.3. Schematic diagram of possible aggregate shapes according to the packing factor, $R_p = v/a_o f_c$, criterion.
Fig. 1.4. Schematic representation of an ellipsoidal micelle. a, b and c are the semi axes.
pH.\textsuperscript{139-143} For example, spherical SDS micelles transform to cylindrical micelles when an electrolyte is added to the solution.\textsuperscript{133,144,145} Chain branching or unsaturation of hydrocarbon tail, particularly cis double bonds, favors cylindrical micelles.\textsuperscript{10,146} Surfactants possessing charged head groups in presence of salts and those having uncharged head groups form cylindrical micelles. Cylindrical micelles can grow in length without limit. In presence of salicylate, CTAB, CPC, \textit{etc.}, can form long worm-like micelles.\textsuperscript{147,148} The size and aggregation number of cylindrical micelles are very sensitive to the surfactant concentration\textsuperscript{149,150} and are usually polydisperse.

\textit{Bilayers and Vesicles}

Bilayers and vesicles are formed by those surfactants that cannot pack into micellar structures due to their small head group area or because their hydrocarbon chains are too bulky to fit into such aggregates. Thus, surfactant molecules with packing parameter $1/2 \leq R_p \leq 1$ form bilayers and this requires that, for the same head group area and chain length, their volume must be twice that of the micelle forming surfactants. Therefore, surfactants with two chains are likely to form bilayers.\textsuperscript{151,152} Bilayers can also accommodate a significantly large number of amphiphile molecules without alteration in the available surface area per amphiphile.

Bilayers are capable of forming spherical vesicles with an internal solvent filled cavity. One bilayer surface is expanded in this process and the other is contracted. This arises since in closed bilayers the energetically unfavorable edges are eliminated at a finite rather than
infinite aggregation number which is also entropically favorable. Thus, so long as the surfactants in curved bilayers can maintain their areas at their optimum values, vesicles are the preferred structures.

Effect of Additives on Structural Transitions

The presence of additives (electrolytes or non-electrolytes) in aqueous surfactant solutions may result in modification of both intramicellar and inter-micellar interactions. Consequently, size, shape, polydispersity, flexibility, and phase structures of ionic micelles may be modified significantly upon the addition of salts. This modification in macroscopic properties of the solution can easily be detected through light scattering or viscosity measurements.

Micellar solutions show a large increase in viscosity on adding salts or organic additives which indicates the growth of the micellar aggregates. The growth of micelles from spherical to cylindrical is of great experimental and theoretical interest. In one of their studies, Hoffmann et al. have shown that at higher concentrations of surfactants the rods shorten when their rotational volumes begin to overlap and undergo another transition to a different anisometric form, probably to that of a disk.

Effect of Salts

When salt is added to aqueous surfactant solution and its concentration reaches a threshold value, rodlike micelles form.
because the presence of salt ions near the polar heads of the surfactant molecules decreases the repulsion force between the head groups. A reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregates, which requires much more space for the hydrophobic chains. Because a spherical micelle has a small volume, it must change into the rodlike micelle to increase the volume/surface ratio. The existence of rodlike micelles was inferred from experiments of light scattering\textsuperscript{134,158,162,163} and confirmed by direct observation under the electron microscope for some systems.\textsuperscript{164-166}

Addition of salts generally found to facilitate the transition. Many workers have discussed the effects of salts on ionic surfactant solutions in terms of electrostatic interactions, ionic hydratability, changes in water structure, \textit{etc.}, and have classified ions as water structure breakers and water structure makers.\textsuperscript{111,167-171}

Counterion effects in micelles,\textsuperscript{172} vesicles,\textsuperscript{6} and DNA\textsuperscript{173} show different affinity orders indicating that significant differences exist in the balance of forces responsible for ion-binding in these aggregates. In general, less hydrated ions lead to higher counterion binding in the surfactant aggregate\textsuperscript{174} and promote micellar growth. Several reports indicate that change from Li\textsuperscript{+} to Cs\textsuperscript{+} induces micellar growth which is related to hydration of specific counterion.\textsuperscript{40,175-177}

Compared to these alkali metal counterions, symmetrical quaternary ammonium ions (F\textsubscript{4}N\textsuperscript{+}) are essentially less hydrated and, therefore,
binding with the micelle will be favorable. On the other hand, R₄N⁺ has a low charge density and may also try to intercalate between head groups of anionic micelles. This will decrease the electrostatic interactions in addition to increased hydrophobic interactions. The positive charge on N-atom will decrease the effective area. All these factors will contribute towards micellar growth.¹⁴⁵

Many experimental studies of salt effects on the structural transitions of micelles have been conducted in the past.¹⁵⁷,¹⁷⁸-¹⁸⁰ Zhao and Fung¹⁸¹ carried out ¹H NMR experiments in order to study the transformation of SDS micelles in presence of NaCl. They found that in the absence of added electrolyte above the cmc spherical micelles are formed. At higher surfactant concentrations, spherical micelles transform into ellipsoidal micelles. In the presence of salt above a threshold concentration, both spherical and ellipsoidal micelles can change into rodlike micelles.

Beneddouch et al.¹⁸² made a series of SANS measurements on micellar solutions of lithium dodecyl sulfate (LDS) as a function of surfactant and salt concentrations. In an electrolyte free aqueous LDS solution the micelles still assume their smallest spherical size (n = 53) for a concentration of up to 0.037 M, whereas the particle shape changes from a sphere to a prolate ellipsoid to accommodate larger n. At low LDS (< 0.3 M) and salt (< 0.5 M) concentrations the growth behavior of micelles was said to be somewhat similar to that of SDS as studied by Missel et al.¹⁸³ who found that the micellar size is a very sensitive
function of [surfactant], temperature and [NaCl]. But at high salt concentrations, there is no evidence of sphere-to-rod transition in contrast to the SDS case. The LDS micelles grow only to a limited extent and thus the assumption of monodispersity is probably valid.

Ikeda et al.\textsuperscript{184} measured light scattering from aqueous solutions of SDS in the presence of 0.8 M NaX (X : F\textsuperscript{−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}, or SCN\textsuperscript{−}) at 35 °C. They found that the molecular weight of the rodlike micelles depends on the cation species of added salt and changes in the order of the lyotropic series of halide ions except for SCN\textsuperscript{−} ion : NaSCN < NaF < NaCl < NaBr < NaI. The difference in micelle size must be caused by the effect of cation species on hydrophobic interaction in the micelle formation or the extent of destruction of the hydrogen bonded structure of water. Huisman\textsuperscript{185} determined the micelle molecular weight of SDS at low concentrations of NaX and he found that the apparent weight average molecular weight of the spherical micelle was dependent on the cation species of added salt but was in the order opposite to that found for the rodlike micelles : NaF > NaCl > NaBr > NaI.

Among cationic surfactants, the salt-induced formation of rodlike micelles of alkyltrimethylammonium bromides in aqueous salt solutions was reported for dodecyl,\textsuperscript{163,186} tetradecyl,\textsuperscript{127,139,187-189} and hexadecyl\textsuperscript{158,189-192} derivatives by measuring light scattering,\textsuperscript{127,139,158,163,187,188,191-194} flow birefringence,\textsuperscript{187,161,195,196} viscosity,\textsuperscript{127} solubilization,\textsuperscript{186,189} \textsuperscript{1}H NMR,\textsuperscript{197,198} SANS,\textsuperscript{199-202} and electron microscopy.\textsuperscript{203,204} Results of light scattering measurements showed that
the sphere-to-rod transition of the micelles took place in aqueous NaBr solutions of dodecyltrimethylammonium bromide at [NaBr] > 1.8 M.\textsuperscript{163}

As halide counterions bind moderately to cationic surfactant aggregates, micellar growth is gradual. Upon changing of the counterion to aromatic ones which usually display higher counterion binding, micellar growth occurs at low surfactant and counterion concentrations.\textsuperscript{141,158,205} However, not only high counterion binding is a prerequisite for micellar growth, but also the orientation of substituents on the aromatic ring is important.\textsuperscript{141,205,206}

Theoretical studies showed that worm-like micelles are long and flexible and that they undergo transformations on relatively short time scales.\textsuperscript{207} This was confirmed by negative staining\textsuperscript{208} and cryo-transmission electron microscopy (cryo-TEM)\textsuperscript{209} which showed that worm-like micelles can become several hundreds of angstroms in length. The presence of worm-like micelles in aqueous solution is often reflected by an increase in relative viscosity.\textsuperscript{210} Upon increase in surfactant concentration, an entangled network of worm-like micelles is formed which displays viscoelastic behavior.\textsuperscript{211} Upon increase of the size of the hydrophobic portion of the counterion the formation of vesicles has been observed.

Porte \textit{et al.}\textsuperscript{212} performed quasi-elastic light scattering (QELS) spectroscopy on cetylpyridinium chloride or bromide (CPC or CPB) micelles as a function of the added [salt]. CPB micelles were found to
grow steadily with increasing NaBr concentration while CPC micelles retained a minimum size at all NaCl concentrations. Their results also support the idea that elongated micelles might exhibit some flexibility.

Double-tailed amphiphiles usually form bilayer sheets as their most hydrated state allows the molecules to pack only in a lamellar arrangement. Upon closing, the bilayers transform to vesicles.\textsuperscript{213-215} Lamellar aggregates are also formed from delicate mixtures of anionic and cationic surfactants in water\textsuperscript{216} or mixtures of ionic surfactants and long chain alcohols in water\textsuperscript{217,218} or electrolyte solution.\textsuperscript{219} Some surfactant molecules in aqueous solution are spontaneously transformed from micelles into a lamellar array in the presence of high salt concentration. The induction of a lamellar arrangement of surfactant molecules by salts finds an important commercial application in liquid laundry detergents.\textsuperscript{220-223}

\textit{Effect of Organic Additives}

Aqueous micellar solutions are known to solubilize water insoluble or slightly soluble organic compounds. In order to improve their properties surfactants are used in presence of additives. (Alcohols are the most commonly used cosurfactants. Cosurfactants are said to be surfactants too weak to form micelles because either their solubility in water is lower than the cmc they would show, had they been sufficiently soluble, or the interaction between their hydrophobic moieties is too weak.\textsuperscript{224} From a practical point of view, alcohols have been used in tertiary oil recovery because they bring about a large decrease of the
viscosity of the micellar systems used in this process.\textsuperscript{225} Addition of alcohols to the solution of an ionic surfactant affects the micellar properties by changing the structure of the solvent and of the surfactant aggregates. It has been shown that the addition of short and medium chain alcohols to aqueous surfactant solutions leads to a decrease in micellar size, whereas long chain alcohols have the opposite effect.\textsuperscript{226-228} Many techniques like $^1$H NMR,\textsuperscript{229} EPR and electron spin echo modulation\textsuperscript{230-232} and neutron scattering\textsuperscript{233} have been used to obtain information about the solubilization of alcohols in micelles. It has been suggested that the short chain alcohols are localized mainly in the aqueous phase, thus influencing the micellar structure by altering the organization of solvent molecules.

Medium chain length alcohols are distributed between the two phases (i.e., micelle and bulk water) and long chain length alcohols are appreciably localized in the micellar phase.\textsuperscript{234,235} In the case of spherical micelles the alcohol is presumably distributed uniformly in the palisade layer. In the case of anisotropic micelles such may not be the case. A neutron scattering study of potassium laurate-decanol-water system showed that the potassium laurate concentration was higher in the rim of the disk than in its central core, the reverse holding for the alcohol.\textsuperscript{236}

Mukerjee\textsuperscript{237} proposed that an additive which is surface active to a hydrocarbon-water interface will be mainly solubilized at the micellar surface[and will be found to promote the]sphere-to-rod transition. Amines are more surface active than alcohols at the air-water interface.\textsuperscript{238} Also, $C_4$ to $C_{10}$ $n$-alkylamines have been found to be solubilized in CTAB and
SDS micelles by hydrophobic and electrostatic effects, and the amine group is left on the surface of the micelle.\textsuperscript{239} These solubilized amines have been reported to form mixed micelles with ionic surfactants.\textsuperscript{240,241} Also, Lindemuth and Bertrand\textsuperscript{64} observed that amines were more effective in the SDS system than in tetracetyltrimethylammonium bromide (TTAB). This indicates a specific interaction between the amine and anionic head group at the micellar interface.

Reekmans \textit{et al.}\textsuperscript{242} have investigated the influence of alkanes and alcohols on the aggregation behavior of anionic surfactants by fluorescence quenching. They used \textit{n}-alkylpyridinium chlorides (C\textsubscript{10} and C\textsubscript{14}) as quenchers and 1-methylpyrene as the fluorescence probe. They have shown that the aggregation number increased on addition of alkanes and higher alcohols. Smith and Alexander\textsuperscript{243} have found from sedimentation and viscosity studies that methylcyclohexane when added to solutions containing CPC increases the aggregation number and viscosity only slightly and regularly, while addition of aromatic additives like toluene and trichlorobenzene showed large increases of viscosity and aggregation number. These results were interpreted in terms of aromatic hydrocarbons' ability to promote rod formation while aliphatic hydrocarbons simply swell the pre-existing spherical micelles. Similar effects were found for benzene and cyclohexane with CTAB.\textsuperscript{244,245}

Eriksson and Gillberg\textsuperscript{245} have determined resonance line shifts and relative line widths of hydrogens for CTAB and aromatic solubilizates at
several solubilize concentrations in 0.1729 M CTAB solution. The results indicate that for benzene, N,N-dimethylaniline and nitrobenzene, the predominating solubilization mechanism at low and intermediate solubilize concentrations involves adsorption at the micelle-water interface whereas *iso*-propylbenzene and cyclohexane are preferentially solubilized in the hydrocarbon part of the micelles. The phenomenon of solubilization of aromatic compounds by adsorption at the micelle-water interface can be understood on the basis of thermodynamic arguments. In aqueous micellar solution a few water molecules penetrate into outer part of the hydrocarbon core of the micelle which is close to the polar heads. It is certainly favorable from an energetic point of view that an aromatic like benzene, N, N-dimethylaniline, or nitrobenzene is substituted for this penetrating water because of the high polarizability of the aromatic ring and the bonding abilities of the substituent groups. Thus, by this adsorption, the system can lower its energy in comparison with the case of an even distribution of aromatic molecules within the micelle, and the energy difference in question may more than compensate the associated diminution of entropy. In the case of *iso*-propylbenzene it is unlikely that the same solubilization mechanism is so effective because of the presence of the *iso*-propyl group, which counteracts the effect of the aromatic ring. Instead, dissolution of *iso*-propylbenzene in the central part of the micelle appears to be energetically advantageous, implying that the particular interfacial structure which promotes a more well-ordered micelle state is never created. This solubilization in the centre of the micelle might
involve a reorganization of the micellar structure so that a more spherical micelle is obtained instead of the postulated original rodlike micelle.

For micelles to maintain a spherical form, some of the tails must be able to reach the centre of the micelle. Addition of an aliphatic hydrocarbon, generally thought to reside in the micellar interior, relieves this requirement. Now the association structure can maintain spherical form containing the solubilized oil at a radius which was previously prohibitive. It is in this manner that the aliphatic hydrocarbons retard the sphere-to-rod transition. Aromatic additives clearly behave differently in the cationic surfactant systems than they do with anionic ones. Aromatic hydrocarbons stimulate micellar growth in the case of cationic surfactants which may stem from interaction of the delocalized π-electron cloud of the benzene ring with the positive charges of the surfactant head groups; a behavior very similar to that of a cosurfactant or counterion. The resulting reduction of head group repulsion favors rods by shrinking the surface area occupied per amphiphile, allowing the aggregation number to increase.

Spherical to worm-like micellar transitions were observed when methylsalicylic acid or hydroxybenzoic acid was added to aqueous CTAB solution. Lin et al. used the combination of shear rheometry and cryo-TEM to investigate the relationship between the colloid microstructures and rheology as a function of acid concentration. Cryo-TEM micrographs show that the sphere to worm-like micelle transition is
not abrupt. The worm-like micelles entangle with each other and the solutions exhibit viscoelastic behavior. They have interpreted this behavior in terms of decrease of the effective area of the hydrophilic head group by association with the carboxylic acid group and increase of the effective area of hydrocarbon chain due to penetration of the phenyl moiety of the acid. They concluded that increasing the effective area of the hydrocarbon chain is an important factor in the transition mechanism.

**Synergistic Effect of Organics + Salt Additions**

Micellar growth is generally facilitated by addition of electrolytes and cosurfactants but Missel et al.\textsuperscript{126} found that urea retards the growth of SDS micelles in 0.8 M NaCl. Low values of the mean aggregation number of SDS in aqueous solutions of \( n \)-pentanol have been found in several studies.\textsuperscript{101,227,246} However, addition of 0.1 M NaCl to solutions of SDS in pure water and to aqueous 0.2 M SDS + 0.6 M \( n \)-pentanol has been found to increase \( n \) from 65 to 93\textsuperscript{246,247} and 47 to 197,\textsuperscript{101} respectively. Thus a large increase of \( n \) is observed in SDS + \( n \)-pentanol "mixed micelles" upon addition of 0.1 M NaCl compared to pure aqueous SDS solution.

In most of the studies\textsuperscript{113,127,248-255} involving, for instance, viscosity,\textsuperscript{113,249,252,254,255} light scattering\textsuperscript{127,210,250-252} and fluorescence probing,\textsuperscript{101,254} changes of micelle shape upon addition of alcohols both in the presence and absence of salts have been reported.

Guerin and Bellocq\textsuperscript{256} have shown that various phases and critical points are present in the system SDS/\( n \)-pentanol/water/NaCl depending on NaCl concentrations and temperature.
Stephany et al.\textsuperscript{257} studied the same system using light scattering techniques with varying concentration of the electrolyte (NaCl). They varied the concentration of \( n \)-pentanol for each NaCl concentration. Data show characteristics of a continuous sphere-to-rod transition. From the results it was concluded that the micelles can be modeled as flexible worm-like objects.

The effect of addition of \( n \)-alcohols on the viscosity of CTAB\textsuperscript{113} and SDS\textsuperscript{258} in presence of KBr and NaBr, respectively, were studied by capillary viscosity method. With CTAB, Prasad and Singh\textsuperscript{113} found that the lower alcohols (C\textsubscript{2} and C\textsubscript{3}OH) decreased the viscosity of CTAB solution in presence of 0.1 M KBr right from the beginning, while C\textsubscript{4}, C\textsubscript{5} and C\textsubscript{6}OH in low concentrations were found to increase the viscosities. Depending on the nature of the alcohol, further addition either made the solution turbid or lowered the viscosity of the solutions. They interpreted the results in terms of the possible transition of micellar shape from rod-to-sphere or elongated rods in presence of added alcohols. When propanol was added to SDS in presence of 0.3 M NaBr,\textsuperscript{258} the viscosity remained almost constant and then decreased, whereas with hexanol it increased continuously. With C\textsubscript{4} and C\textsubscript{5}OH, depending on the concentration, increase followed by a decrease in viscosity was observed. The behavior was interpreted in terms of solubility of alcohols in various solubilization regions of the micelle with a resultant change in \( R_p \) of the "effective surfactant" (\textit{i.e.}, SDS + \( n \)-alcohols). As regards the effect of temperature on the system, an increase in temperature caused a decrease in viscosity, which was related to micellar breakdown.
Kabir-ud-Din and co-workers have studied the effect of addition of amines, \textsuperscript{115,116,259-262} alcohols, \textsuperscript{116,258,259,261,262} and hydrocarbons\textsuperscript{263,264} to ionic micellar solutions with or without salts. Increase or decrease in viscosities of the solutions were found to be dependent on the chain length and nature of the additive. The results were explained in view of structural transitions. Similar transitions of micellar shape by the addition of lower alcohols to DTAB/NaSal micelles have been reported from light scattering measurements.\textsuperscript{265}

**Importance of the Research Problem**

For the past four decades a considerable amount of research effort has been directed towards determining the physicochemical properties of self-assembled surfactant aggregates, especially, micelles and unilamellar vesicles. Although many reasons can be cited for the widespread interest in elucidating the physicochemical properties of micelles and vesicles, there are primarily three reasons. Firstly, one can consistently and easily prepare aqueous micellar and vesicular solutions which have aggregates of colloidal dimensions with characteristic size, shape and surface properties. Hence micellar and vesicular systems have been employed as model systems in investigations concerned with understanding colloidal physicochemical phenomena.\textsuperscript{4,266} Secondly, the similarities between self-assembled surfactant aggregates, such as micelles and vesicles, and biological lipid membranes have not gone unnoticed. Thus, in many studies micelles and vesicles have served as rudimentary model systems
for biological lipid membrane systems.\textsuperscript{3,266} Thirdly, it has been found that micelles and vesicles can act as unique reaction media. Indeed, solubilization of reactants within self-assembled surfactant aggregates frequently leads to altered reaction rates, reaction routes and stereochemistries.\textsuperscript{3,266} Obviously, micelles and vesicles cannot be fully exploited as reaction media until all their physicochemical properties have been ascertained.

(An increase in our understanding of physicochemical properties of mixed surfactants (or surfactant + additive) is of great theoretical and practical importance, since pure, single surfactants are rarely used in applications. Studies on surfactants and their mixtures with variety of additives in aqueous solutions are of interest for fundamental understanding of their interactions with regards to their chemical, pharmaceutical, mineral processing, petroleum engineering,\textsuperscript{267-273} household and technical applications,\textsuperscript{274-276} cloud-point extraction technique (CPET),\textsuperscript{277,278} and hydrophobic interaction chromatography.\textsuperscript{279})

Micellar solutions are called 'compartmentalized liquids', the micelles serving as compartments which can help dissolution of polar and nonpolar compounds in normal and reverse micellar solutions, respectively. This is an advantage which is not achieved otherwise. Solubilization and dispersion\textsuperscript{280} are two important uses of micellar solutions. This is relevant in many biological processes.\textsuperscript{266,267,281-283}

From a practical point of view, the presence of non spherical micelles gives solutions a very high viscosity which might be of importance in
industrial formulations as it enhances performance and customer appeal of formulations. Control of viscosity of preparations with nonionic surfactants can be done by varying the length of the hydrophilic head group.

Solubilization of organics in aqueous solutions of surfactants could be useful in micellar enhanced ultrafiltration. In this process, such system is added to a polluted aqueous solution. The surfactant is then mainly in aggregate form which can solubilize the organic solute. Since the size of the micelles is greater than that of the dissolved organics, the micellar solution can be filtered with an ultrafiltration membrane having pores small enough to reject the aggregates containing the organic pollutants.

Due to reasons mentioned above and many more, the effect of additives on the properties of aqueous surfactant solutions has been a subject of intense research. This thesis is exclusively devoted to studying the effect of a variety of additives on the solution properties of an anionic surfactant, viz., SDS.

Whereas abundant literature is available on studies performed on surfactant + salt or surfactant + organic additive systems, that on surfactants in simultaneous presence of salts and organics is scanty. However, the available studies show that in some concentration ranges of salts and organics, there exists a kind of synergism (e.g., drastic changes in viscosity). In this thesis systematic studies on such
synergism and its effect on solution behavior are described. Additionally, quaternary salts were used to see the effect in place of routinely used inorganic salts.

Layout of the Thesis

Keeping the view presented in the last paragraph, the work was planned in a manner to find the micellar morphology of SDS solutions in presence of quaternary ammonium salts (R₄NBr) and then the effect of organics was combined in the latter part. The thesis consists of five chapters including the present one. As evident, this chapter is mainly concerned with the General Introduction of the research problem including the lacunas where the need of more research was felt.

The Chapter II includes the material and methodologies which were used in the studies. Individual purity, conditions of storage, etc., are also pointed out.

SANS studies in presence of R₄NBr (R = C₂H₅, n-C₃H₇) were performed to see the effect of concentration and alkyl chain length of the salt on micellar shape and size. Aggregation number (n), effective charge per monomer, (α) and semi-major to semi-minor axis ratio (c/a) were computed and the data are compared with simple inorganic salt results reported in the literature. These SANS study data are contained in Chapter III.

Effect of adding aliphatic amines in the presence of quaternary bromides in anionic SDS micellar solutions was studied viscometrically. This work is included in Chapter IV. The work describes effect of alkyl
chain lengths of quaternary bromides and amines as well as of their concentration variation.

Looking for solubilization regions and their changes in presence of salts have been the reasons for carrying out studies described in Chapter V. Aliphatic alcohols and aliphatic and aromatic hydrocarbons were chosen as the organic additives (solubilizates) and $R_4NBr$ ($R =$ H, CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, n-C$_4$H$_9$, n-C$_5$H$_{11}$) as the salts.