Chapter-I

General Introduction
Understanding the physicochemical properties of self-assembling systems of amphiphilic molecules in aqueous solution is relevant for many fields of pure and applied science.¹

A surfactant (an abbreviation for surface active agent) is a surface active amphiphile that aggregates (self-assembles) in water or other solvent to form various microstructures. They are able to modify the interfacial properties of the liquid (nonaqueous or aqueous) in which they are present.

Surfactants are ubiquitous materials, which exhibit a fascinating range of applications in chemical processes, industries, in the formulation of pharmaceuticals, in mineral processing technologies, and in food processing industries.²⁶

**Surfactants and their Classification**

A surfactant molecule consists of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and one which is insoluble (the lyophobic part). When the fluid is water these parts are known as the hydrophilic and hydrophobic, respectively. The hydrophilic part is referred to as the head group and the hydrophobic part as the tail (Fig. 1.1). Most of the surfactants have a long hydrocarbon tail that can be linear or branched and interacts only very weakly with the water molecules in an aqueous environment. The hydrophilic

![Fig.1.1– Schematic illustration of a surfactant monomer.](image-url)
head is a relatively small ionic or polar group that interacts strongly with water via dipole-dipole or ion-dipole interactions. Hence, a surfactant can be said to have a split personality, as it is composed of two parts with entirely different tendencies. Because of this unusual amphipathy property, surfactants are very versatile substances.

The classification of surfactants is made on the basis of the charge of the polar head group. The surfactant may be classed as ionic, zwitterionic, and nonionic.

1. Ionic surfactants: Surfactants belonging to this class contain either an anionic or a cationic charge under normal conditions.
   (a) Anionic - The surface-active portion of the molecule bears a negative charge. Anionic surfactants are the most widely used class of surfactants in industrial applications. Due to their low cost of manufacture, they are used in practically every type of detergent.
   (b) Cationic - The surface-active portion of the molecule bears a positive charge. The prime use of cationic surfactants is their tendency to adsorb on negatively charged surfaces, e.g., anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents, fabric softeners, hair conditioners, antistatic agent, for fertilizers, and as bactericides.

2. Zwitterionic surfactants: Zwitterionic (amphoteric) surfactants comprise a long hydrocarbon chain attached to a hydrophilic polar head containing both positive and negative charges, which give it the properties of zwitterions and thus lead to head group hydrophilicity an intermediate between that of ionic and nonionic surfactants. Zwitterionic surfactants have excellent dermatological properties as they are less irritating to skin than many ionic surfactants and have thus useful applications when combined with ionic and nonionic surfactants in cosmetics and pharmaceutical industries.

3. Nonionic surfactants: The surface-active portion of the molecule bears no apparent ionic charge. Nonionic surfactants are second to anionics in cleaning applications. An important group of nonionic surfactants includes those where
the hydrophilic portion comprises a chain of ethoxy group and is known as ethoxylates.\textsuperscript{12,13}

Examples of different types of surfactants are given in Table 1.1.

\textbf{Micellization and Micellar Parameters}

The parameter of greatest fundamental value is the critical micelle concentration (cmc). When surfactants are dissolved in water at low concentrations, physical properties of solutions, such as surface tension, conductance, vapor pressure, and turbidity indicate that little or no aggregation of surfactant occurs. However, as the concentration is increased the behavior of such properties, and that of many others, changes dramatically over a relatively narrow range of concentrations. Such changes are attributed to the sudden onset of molecular aggregation (\textit{micellization}) and such aggregates are termed as \textit{micelles}. The range of concentrations within which this occurs may be termed as critical micellar region\textsuperscript{14}. It is common practice to choose a concentration in this region and call it the \textit{critical micelle concentration (cmc)}. Several experimental methods have been used to determine the cmc. Some other techniques frequently used to identify the cmc are interference refractometry\textsuperscript{15}, solubilization\textsuperscript{16}, flourimetry\textsuperscript{17}, light scattering\textsuperscript{18}, \textsuperscript{1}H NMR\textsuperscript{19}, etc.

The various factors that determine the concentrations at which micelles form are listed below.

\textbf{Hydrophobic group} : The cmc decreases strongly with increasing alkyl chain length of the surfactant. While modification to the hydrocarbon chain (such as introducing branching, or double bonds, or polar functional groups along the chain) usually leads to increase in cmc, a dramatic lowering of the cmc (one or two orders of magnitude) results from fluorination of the alkyl chain.

\textbf{Hydrophilic group} : Cationics typically have slightly higher cmc’s than anionics. The cmc’s of nonionics are much lower than for ionics. For some nonionics, there is a moderate increase of the cmc as the polar head becomes larger.
Table 1.1 – Examples of typical surfactants.

<table>
<thead>
<tr>
<th>Type</th>
<th>Structural Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Anionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>CH₃(CH₂)₁₄OSO₂⁻Na⁺</td>
<td>SDS</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>CH₃(CH₂)₁₁C₆H₄SO₃⁻Na⁺</td>
<td>SDBS</td>
</tr>
<tr>
<td>b. Cationic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide</td>
<td>CH₃(CH₂)₁₅(CH₃)₃ N⁺Br⁻</td>
<td>CTAB</td>
</tr>
<tr>
<td>Dodecylpyridinium chloride</td>
<td>CH₃(CH₂)₁₁C₆H₄N⁺Cl⁻</td>
<td>DPC</td>
</tr>
<tr>
<td>2. Zwitterionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Dodecyl-N,N-dimethylglycine</td>
<td>CH₃(CH₂)₁₁N⁺(CH₃)₂CH₂COO⁻</td>
<td>–</td>
</tr>
<tr>
<td>3-(Dimethyl)dodecylammonio)-propane-1-sulfonate</td>
<td>CH₃(CH₂)₁₁N⁺(CH₃)₂CH₂CH₂⁻</td>
<td>–</td>
</tr>
<tr>
<td>3. Nonionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(ethylene glycol)-t-octylphenylether</td>
<td>t-C₇H₁₇-C₆H₄-(OCH₂CH₂)₆OH</td>
<td>TX-100</td>
</tr>
<tr>
<td>Polyoxyethylene(6) dodecanol</td>
<td>CH₃(CH₂)₁₁(CH₂CH₂O)₆OH</td>
<td>–</td>
</tr>
</tbody>
</table>
**Counterions in ionic surfactants**: Monovalent inorganic counterions give roughly the same cmc but, increasing the valency to 2, gives a reduction of the cmc by roughly a factor of 4. Organic counterions reduce the cmc compared to inorganic ones, the more so the larger the nonpolar part. Increased binding of counterion, in aqueous system, causes a decrease in the cmc of the surfactant.

**Temperature**: Numerous changes in cmc with temperature are known which paint a complex picture. Very few of these take place above 100 °C, however, and studies of the effects of temperature on micellization have mostly been limited to lower temperatures. The cmc of surfactants generally passes through a minimum with increasing temperature. The apparent entropy change of micellization (which is based only on a cmc change with temperature) decreases from a positive value to a negative one (at the temperature of minimum cmc) with increasing temperature.

**Pressure**: Many reports have appeared on the effect of pressure on micelle formation for ionic and nonionic surfactants\textsuperscript{20,21}. The cmc of ionic surfactants increases up to 100 MPa followed by a decrease above this pressure due to an increase in the dielectric constant of water, solidification of the micellar interior\textsuperscript{22}, making less electrical work necessary to bring a monomer into a micelle.

Just as in the case of temperature, data for the variation of cmc for surfactants with pressure also fall on a reduced curve, which passes through a maximum cmc\textsuperscript{*} at pressure $p^*$. Since the volume change on micelle formation can be written as

$$\Delta V_m^o = RT \left( \frac{\partial \ln \text{cmc}}{\partial p} \right)_T,$$

Then $p^*$ is the pressure at which $\Delta V_m^o$ becomes zero.

For nonionic surfactants, the cmc values increase monotonously and then level off with increasing pressure.

**Electrolyte**: Adding an indifferent electrolyte to a surfactant solution has a pronounced effect on the cmc, especially for ionic ones. For nonionic surfactants, the effect is smaller but still significant and the difference between
the two is dramatically demonstrated by the difference in the functional
dependence of cmc on salt concentration, $c$:

$$\log (\text{cmc}) = b_1 + b_2 c \text{ (nonionic)} \quad (1.2)$$

and

$$\log (\text{cmc}) = b_3 + b_4 \log c \text{ (ionic)} \quad (1.3)$$

The constants, $b_i$, depend upon the nature of the electrolyte.

For the ionic surfactants, the principal effect of the salt is to partially
screen the electrostatic repulsion between the head groups and so lower the
cmc. The effect of salts of the same valence type are usually discussed in terms
of the lyotropic series. For the nonionic ones the concentrations of salts
required to produce significant effects are much higher and the discussion of
such behavior introduces the notion of *'salting-in'* and *'salting-out'* of
nonelectrolytes by the electrolyte$^{24}$.

**Solvent medium**: Nonpolar medium offers environment similar to the
surfactant tail so that the tendency of self-association is reduced.

**Organic additive**: Addition of organic compounds affect the cmc either by
penetrating into the micellar region, or by modifying solvent-micelle or
solvent-monomer interactions.

It is common practice to divide organic materials into two main groups.
Group A is composed of molecules (like alcohols with moderate to long
hydrocarbon chains) that appear to be adsorbed in the outer regions of the
micelle, forming a palisade (i.e., fence-like) structure with the surfactant
molecules. This lowers the free energy of micellization to more negative values
and so reduces the cmc. Group A compounds are generally effective at quite
low bulk concentrations. Group B materials alter the cmc at substantially
higher bulk concentrations and probably exert their influence through
modification of the bulk water structure. The effect is usually discussed in
terms of modification of water structure, its dielectric constant, or its solubility
parameter (cohesive energy density).
**Micellar Structure**

The most simple picture of the micelle structure formed by ionic surfactants is the Hartley model\textsuperscript{25}. In this model *micelles* are considered as globular structures having a hydrocarbon core surrounded by a highly hydrophilic region formed by the surfactant head groups, counterions, and water molecules. Several aspects of this self-assembled structure have been the subject of discussion on the basis of which alternative models of micelle structure have been suggested like, Menger model\textsuperscript{26}, Dill-Flory model\textsuperscript{27}, Fromherz model\textsuperscript{28}, etc.

In nonpolar medium surfactants associate to form the so-called *reverse/inverted micelles*. Reverse or inverted micelles have a water core surrounded by the surfactant polar head groups. The alkyl chains together with a nonpolar solvent make up the continuous medium.

When two or more types of surfactants are in solution, a complex balance of intermolecular forces is responsible for the formation of *mixed micelles* against the formation of micelles constituted by surfactant of one type.

For ionic surfactants, as for nonionics, the change in micelle size with increasing surfactant concentration is related to micelle polydispersity. At low surfactant concentrations, the micelles are usually spherical. With increasing surfactant concentration, the morphology spectrum runs from micelles, through a cubic array of micelles, hexagonally packed rods, cubic bicontinuous spheres, to lamellae where phase inversion takes place, and the inverted morphologies develop: cubic, reversed hexagonal, cubic, and reversed micelle\textsuperscript{29,30}. The symmetry and stability of the microstructure depend intimately on chain size and chemistry as well as on physical variables such as temperature. The underlying principle is that two fundamentally different sub-units of the amphiphile are driven to phase separate like oil and water, with the limiting condition that they are covalently attached to each other. Molecules, i.e., macromolecules, are therefore thermodynamically driven to self-assemble in order to minimize the contact between the immiscible components (the solvent and the insoluble block).
The shape of microstructures can be correlated with molecular geometry of the amphiphile predicted on the basis of packing considerations.

**Packing parameter**: The molecular packing parameter is a remarkably simple and insightful parameter to consider when discussing the morphology of the structures formed by surfactants. Packing considerations constitute a factor which involves the nature of the head and tail groups of the surfactant. A critical ratio ($R_p$) with associated limits for several of the possible aggregation shapes has been devised by Ninham et al.\(^1\)

\[ R_p = \frac{v_h}{a_o l_c} \]  \hspace{1cm} (1.4)

where

- $v_h=$ the volume of the amphiphile’s hydrocarbon tail,
- $a_o=$ the optimum cross-sectional area per amphiphile molecule, and
- $l_c=$ the length of the fully extended hydrocarbon tail (see Fig. 1.2).

![Fig.1.2- Schematic illustration of an amphiphile molecule with the volume of amphiphile’s hydrocarbon tail $v_h$, the optimum cross-sectional area per amphiphile molecule $a_o$, and the length of the hydrocarbon tail $l_c$.](image)

The change in micellar structure and size can be achieved by adding solutes. These additives, depending on their mode of action, are divided into the following two groups.

1. **Additives which do not penetrate micelles**: Although a third component added to a micellar solution does not solubilize in the micellar phase, it can
involve different interactions with surfactant which depend on the nature of the additive. We can distinguish the following –

(a) **Strong inorganic electrolytes** which interact with the micelles electrostatically. It is established that the salts present affect strongly the aggregation number of the micelles$^{32-35}$. This fact may be due to the binding of salt counterions to the micellar surface, thus decreasing the repulsion between the polar head groups of surfactant molecules and increasing the local curvature.

(b) **Highly polar nonionic additives** which affect the micellization process through their effect on physicochemical properties of the solvent. The effect is usually discussed in terms of whether the additive is a water structure maker (*kosmotrope*) or a structure breaker (*chaotrope*). Typical *structure makers* are xylose and fructose and *structure breakers* are urea and formamide.

2. **Additives which penetrate micelles**: In the micellar aggregates three sites of solubilization can be identified: the micellar core (highly hydrophobic), the micellar surface (highly hydrophilic), and the palisade layer (the region between the head group and the core). Therefore, depending on the site of solubilization, there are three classes of compounds:

(a) **Apolar additives** which are essentially solubilized in the micellar core. For micelles to maintain a spherical form, some of the tails must be able to reach the center of the micelle. Addition of an aliphatic hydrocarbon, generally thought to reside in the micellar core, relieves this requirement. Now the association structure can maintain spherical form containing the solubilized oil at the radius which was previously prohibitive. So aliphatic hydrocarbons retard the sphere-to-rod transition. If the hydrocarbon core region resembles a not-too-viscous hydrocarbon liquid, one would expect considerable solubilization of benzene and related compounds in this region: on the other hand, the possibility that aromatic $\pi$-electron systems could interact (albeit weakly) with ionic charges and dipoles in the outer regions of the micelle might account for the fact that aromatics interact somewhat more strongly with ionic micelles than do the aliphatic hydrocarbons.$^{36}$
(b) **Polar additives** whose site of solubilization is the palisade layer. Such type of incorporation of an additive into micelle would be expected to increase the mean volume per surfactant molecule \( (v_h) \) without significantly affecting the average head group area \( (a_o) \) and length per surfactant molecule \( (l) \) in the packing parameter. Thus, packing parameter increases when such additives are added to the micellar system and larger micelles are formed.

(c) **Complexes with inorganic ions (crown ether)** which can solubilize at the micellar surface depending on the nature of the surfactants and/or of the complexing molecule.

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**Cloud Point**

Surfactant have mainly been used for the solubilization of organic compounds in water, enhancement of analytical signals, control of reaction paths, micellar catalysis, alteration of spectral features of the reaction products among others. They have also been used for compartmentalization of ionic and natural solutes into very small volumes. This process depends upon a distinctive physical property of surfactants (mainly nonionic ones), namely, the existence of a critical point in the phase separation phenomenon which can be induced by changes in the temperature of the micellar solution. Above this critical point or **cloud point (CP)**, two isotropic phases are well defined: dilute aqueous phase containing a low concentration of surfactant (surfactant-lean phase), and surfactant-rich phase. For ionic surfactants, the phenomenon (more properly, lower consolute phase behavior) rarely occurs presumably because electrostatic repulsion among charged micelles prevents phase separation in most cases.

Clouding is attributed to the dehydration of hydrophilic groups of the amphiphiles. There are many theories to explain the presence of CP. However, it is still not completely resolved. The dehydration of micelles can be achieved either by raising of temperature so that hydration forces give way
to van der Waals attraction\(^4\) or by filling the hydrophilic region with other compounds so that the effective number of water molecules is reduced\(^4\).

Since the phase transition temperature is determined by a very delicate balance between opposing effects, a slight change in the intermicellar interaction potential may affect the cloud temperature considerably.

Several factors have been considered to be responsible for the CP phenomenon like structure of surfactant molecule, concentration, temperature and a third component (additive). CP is very sensitive to the presence of additives in a system, even at very low concentrations. The additives modify the surfactant-solvent interactions, change the cmc, size of micelles and phase behavior in the surfactant solutions\(^4\).

Many efforts have been made to investigate the effect of various additives, e.g., inorganic electrolytes\(^4\), organic compounds\(^4\), ionic surfactants\(^5\), and zwitterionic surfactants, on the CP of a nonionic surfactant. The effect of organic additives on the CP of anionic surfactants can vary widely, depending on the nature of additives\(^5\).

Some authors have also reported the CP of ionic surfactants\(^5\). Raghavan et al.\(^5\) has reported the clouding behavior in ionic surfactants in presence of salts with hydrophobic counterions. The plausible hypothesis given is that the binding of hydrophobic counterions promotes micellar branching. Kabir-ud-Din and coworkers have found that adding salts with large hydrophobic cations to anionic surfactants can lead to clouding when such behavior is absent in the pure surfactant solution\(^5\).

Mahajan et al.\(^6\) observed that the cloud point of both Tween 20 and 80 decreases in the presence of glycol oligomers as well as triblock polymers (TBP). Among the glycol oligomeric additives, ethylene glycol monobutyl ether was found to reduce the CP maximum. An increase in repeating units of polymeric glycol additives leads to a decrease in CP. Reduction in the CP in the presence of TBP depends upon the increase in hydrophobic/hydrophilic ratio among the polypropylene to polyethylene units.
It has been shown that certain mixed surfactant solutions clouded in two stages, first becoming faintly turbid (preclouding) and then fully clouded at a higher temperature.\textsuperscript{64} Older literature references to this phenomenon were limited to brief reports of solution conditions referred to as double cloud point, or an apparent cloud point.

Classical light scattering studies have been interpreted as indicating a rapid increase in micellar aggregation number, with long cylindrical micelles being formed.\textsuperscript{65} However, other interpretation of this phenomenon, and of SANS data, suggest that only a modest growth (if any) in micelle size occurs but that intermicellar interaction increases markedly as the two-phase boundary is approached.

\textbf{Hydrotropy}

The phenomenon of 'hydrotropy' was discovered by Neuberg in 1916\textsuperscript{66}. Hydrotopes are weakly surface-active compounds that can increase the solubility of organic substances in aqueous solution.\textsuperscript{66} Besides enhancing the solubilization of compounds in water, they are known to exhibit influences on surfactant aggregation leading to micelle formation, phase manifestation of multicomponent systems with reference to nanodispersions and conductance percolation, clouding of surfactants and polymers, etc\textsuperscript{67,68}. Hydrotropes are used as solubilizing agents in drug formulations. The biological action of hydrotropes has interested several researchers.

\textbf{Classification of Hydrotropes}

Typical hydrotropes are alkali and alkaline metal salts of benzoates, aromatic sulfonates, substituted phenols, proline, and hydrochloride salts of \textit{p}-amino benzoic acid, substituted anilines, etc. Some typical cationic, anionic, nonionic, and neutral hydrotropes are examplified in Table1.2.
Table 1.2 – Examples of hydrotropes.

<table>
<thead>
<tr>
<th>Type</th>
<th>Structural Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Anionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium salicylate</td>
<td>COO'Na</td>
<td>NaSal</td>
</tr>
<tr>
<td>Sodium p-toluenesulfonate</td>
<td>SO3'Na</td>
<td>NaPTS</td>
</tr>
<tr>
<td>2. Cationic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Toluidine hydrochloride</td>
<td>NH3*Cl</td>
<td>–</td>
</tr>
<tr>
<td>3. Nonionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resorcinol</td>
<td>OH</td>
<td>–</td>
</tr>
<tr>
<td>α-Naphthol</td>
<td>OH</td>
<td>–</td>
</tr>
</tbody>
</table>
A hydrotrope molecule has been regarded as an amphiphilic entity but with less hydrophobic character than the common surfactants, rather like short-chain amphiphiles and the bile salts. They may self-associate in aqueous medium, comparable to amphiphile self-association or micellization. The aggregation numbers found in the case of hydrotropes are expected to be lower compared to those found in the case of micelles. Generally, it has been observed that hydrotropy does not seem to be operative below a particular concentration, while above this concentration the solubilization rises markedly. This concentration above which hydrotropic action is observed may be referred to operationally as the **minimal hydrotropic concentration (MHC)**[^6]. At this concentration other hydrotropic properties such as solubilization become prominent. The extent of hydrotropic solubilization is much higher and selective, while that in case of surfactant solubilization is more general, of lower capacity and less selective.

Hydrotropes exhibit variable influences on microstructures of amphiphile aggregates. The liquid crystalline phase can be transformed into a higher or lower analogue. It may promote as well as inhibit micelle formation and can alter the liquid-liquid phase-separation temperatures of ethoxylated surfactant. In a microemulsion, it alters the solubility region and percolation threshold temperature. Packing requirement in the surfactant monolayer, extensive H-bonding with solvent molecules and the ability of complex formation may explain the selectivity in hydrotrope action. Aromatic hydrotropic salts contain counterions that adsorb on the surface of micelles and thereby decrease their surface charge density. In addition, the coion released by ionization of the hydrotropic salt increases the ionic strength and screens electrostatic interactions[^70-72]. In the majority of the cases transition from spherical to wormlike micelles takes place which corresponds to a drastic increase of elasticity and viscosity of the fluid. Such viscoelastic wormlike micelles have attracted much interest in fundamental research and practical applications.
Although physicochemical investigations on solution properties of hydrotropes have well-passed their infancy, further work is required to rationalize the phenomena encountered.

Relevance of the Research Problem

The transition of proteins from an unfolded state to the folded one has some resemblance to micelle formation. For several years, continuing efforts have been made to understand the effect of urea and other denaturants on the stability of proteins in aqueous solution. Related efforts to understand urea’s effects on the property of surfactant aggregates, particularly aqueous micelles, are also ongoing because the same basic intermolecular and ionic forces control both surfactant aggregate and protein stabilities. Nevertheless, because this urea effect involves a number of complex factors, there are currently certain controversies for elucidating the mechanism by which this process takes place.

Micelles are attractive as models, not only for their simplicity but because hydrophobic interaction can be assessed relatively easily by observing the phenomenon of micellization or sphere-to-rod transition (s→r). From 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. For ionic surfactants, such variation in viscosity may be caused by salt addition or solubilization.

Cloud point is an important property of surfactants and is used in applications such as detergency since (a) adsorption of surfactants on substrates has been found to increase significantly near their cloud points, and (b) oily soil removal from substrates is optimized at the cloud point.

The practical importance of CP lies in the fact that suspensions, emulsions, and ointments, stabilized with nonionic surfactants, become
unstable when heated in the vicinity of CP, e.g., during steam sterilization or some end use.

Hydrotropes are a special class of compounds that exhibit distinct solution properties. They are efficient solubilizers. Besides solubilization, hydrotropes have uses in vesicle preparation and selective separation as stabilizer of o/w microemulsion, viscosity modifiers and as cleaning agents in cloudy detergent formulation. Although there are evidences in favor of self-association of hydrotropes, conclusive evidence in favor of MHC and clear information on the nature of aggregation are still lacking.

**Layout of the Thesis**

This thesis consists of five chapters including this one which is concerned mainly with the general introduction of amphiphiles, the factors responsible for the various aggregation patterns and their solution properties, e.g., cloud point phenomenon, etc.

In **Chapter II**, the methodologies which were used in the studies are detailed. Materials used, individual purity, make, etc., are also given in tabular form.

**Chapter III** consists the effect of addition of urea and other family members on micellization and the related phenomena like sphere-to-rod transition in a typical ionic micellar solution (SDS) and its possible implications in protein folding. Conductivity, viscosity and small-angle neutron scattering (SANS) measurements have been performed to gain insight in the phenomenon and changes in the morphology involved. CP variation of TX-100 at different concentrations of urea show that urea acts as an ameliorator for micellization up to a certain concentration.

Studies on the effect of various non-aqueous solvents on the CP behavior of ionic SDS containing different salts are described in **Chapter IV**.

**Chapter V** contains the work performed on the association of hydrotopic compound sodium salicylate (NaSal) in presence of different additives.
References


