General Introduction
Surfactants and Surfactant Micelles

"Surfactants", a happy and convenient contraction of "surface active agents", owe their name to their interesting behavior at surfaces and interfaces. When present at low concentration in a system, they have the property of adsorbing onto the surfaces or interfaces of the system and the adsorption of surfactant lowers the interfacial tension between phases. Because of their ability to lower interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents and so forth.

Surfactants have a characteristic of amphipathy: the molecules have two distinct parts; one that has an affinity for the solvent and the other that does not. Hence, a surfactant can be said to have ‘split personality’, because it is composed of two parts of entirely different tendencies. In aqueous solutions, these two moieties are hydrophilic and hydrophobic, respectively. Often the hydrophilic part of the molecule is simply called the ‘head’ and the hydrophobic part—usually including an elongated alkyl substituent— is called the ‘tail’. The amphipathic structure of the surfactant causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with
its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it. It is the tendency for the hydrophobic parts of the molecules to aggregate because of mutual dislike of the solvent which is the driving force for surfactant self-association.

The chemical structures of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such as water, the lyophobic group may be a hydrocarbon or fluorocarbon or siloxane chain of proper length, whereas in less polar solvent only some of these may be suitable (e.g., fluorocarbon or siloxane chains in polypropylene glycol). In a polar solvent such as water, ionic or highly polar groups may act as lyophilic groups, whereas in a nonpolar solvent such as heptane they may act as lyophobic groups. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modifications in the structure of the lyophobic and lyophilic groups may become necessary to maintain surface activity at a suitable level. Thus, for surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic in that solvent under the conditions of use.
Classification of Surfactants: Surfactants are classified on the basis of the charge carried by the polar head group as:

**Anionic.** The surface-active portion of the molecule bears a negative charge, for example, \(\text{RCOO}^-\text{Na}^+\) (soap), \(\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+\) (alkylbenzene sulfonate).

**Cationic.** The surface-active portion bears a positive charge, for example, \(\text{RNH}_3^+\text{Cl}^-\) (salt of a long-chain amine), \(\text{RN}(\text{CH}_3)_3^+\text{Cl}^-\) (quaternary ammonium chloride).

**Zwitterionic.** Both positive and negative charges may be present in the surface-active portion, for example, \(\text{RN}^+\text{H}_3\text{CH}_2\text{COO}^-\) (long-chain amino acid), \(\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-\) (sulfobetaine).

**Nonionic.** The surface-active portion bears no apparent ionic charge, for example, \(\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}\) (monoglyceride of long chain fatty acid), \(\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)\text{x}OH\) (polyoxyethylenated alkylphenol).

**Gemini.** Gemini\(^{1,2}\) surfactants are defined as surfactants made up of two identical amphiphilic moieties connected at the level of the head groups, by a spacer group which can be hydrophilic or hydrophobic, rigid or flexible (Fig. 2).\(^3\) Thus, an ionic gemini has in sequence a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail.
A schematic representation of gemini is given in Fig. 1.1.

\[ \text{Fig. 1.1. Schematic representation of gemini surfactants.} \]

Geminis were known long before to Bunton et al.,\textsuperscript{4} who studied the catalysis of nucleophilic substitutions by "dicationic detergents", to Devinsky et al.,\textsuperscript{5} who reported on the surface activity and micelle formation of some new "bisquaternary ammonium salts", and to Okahara et al.,\textsuperscript{6} who prepared and examined "amphipathic compounds with two sulphate groups and two lipophilic alkyl chains". Later in 1991, Menger and Littau\textsuperscript{1} assigned the name "gemini" to bis-surfactants with rigid spacer (i.e., benzene, stillbene).

Geminis can have unusual and exceptional structural features. The relevant structure features include:

(a) All geminis possess at least two hydrophobic chains and two ionic or polar groups.

(b) A great deal of variation exists in the nature of the spacer, which can be short (2 methylene groups) or long (12 methylene groups); rigid (stillbene) or flexible (methylene chain); and polar (polyether) or nonpolar (aliphatic, aromatic).
The polar group can be positive (ammonium), negative (phosphate, sulfate, carboxylate), or nonionic (polyether, sugar).  

Although the great majority of geminis have two identical polar groups and two identical chains, unsymmetric geminis are known.

"Geminis" with three or more polar groups or tails have been synthesized.

Gemini surfactants attract current attention in the area of surfactant science because of the number of unique properties that they manifest. For instance, they have been used in various purposes such as the preparation of high porosity materials, analytical separations, solubilization processes, skin care formulations, antibacterial regimens, and anti-pollution protocols. Also, these surfactants manifest lower critical micelle concentration (cmc), higher viscoelasticity and enhanced propensity for lowering the oil-water interfacial tension in comparison with their conventional counterparts bearing single head group and single lipophilic chain. Micellar morphologies and properties of gemini surfactants depend strongly on the nature as well as the length of the spacer. The type of headgroups in the gemini surfactants also influences their aggregation properties.

Thus, keeping in view the importance of these novel type of surfactants, the geminis, this thesis delves into such topics as critical micelle
concentration, aggregate size and shape, and catalytic role of geminis towards ninhydrin-amino acid reactions.

**Micelle Formation:** One of the most characteristic properties of amphiphilic molecules is their capacity to aggregate in solutions. The aggregation process depends of course, on the amphiphilic species and the condition of the system in which they are dissolved. The narrow concentration range over which surfactant solutions show an abrupt change (Fig. 1.2) in physicochemical properties is called the critical concentration for the formation of micelle or 'critical micelle concentration' (cmc). \(^{19-21}\) cmc values for commonly used surfactants range from about \(10^{-4}\) to \(10^{-2}\) M. \(^{22,23}\) Term cmc was established by Bury,\(^{24}\) defining it as a concentration range below which surfactant is in solution as monomer and above which practically all additional surfactant added to the solution forms micelles. Just above the cmc, micellar structure is considered to be roughly globular or spherical.\(^{22,23}\) A schematic representation of such a structure is given in Fig. 1.3. However, the exact structure of micelles is still somewhat controversial. There is evidence, for example, that micelles have a rough surface with considerable penetration of water between head groups.\(^{23}\)
Fig. 1.2. Variation of physical properties with surfactant concentrations.
Although an oversimplification, Fig. 1.3 is a useful model for qualitative understanding of experimental results. Hydrophobic cores of micelles have diameters of about 10-30 Å. The charged coat of ionic micelles, called the Stern layer, is usually 60-90% neutralized by counterions in aqueous surfactant solutions without added salt. The surface charge of ionic micelles results in an electrical potential on the order of 100mV at the micellar-water interface with the same sign as the surfactant head group. If salt is added to the solution, the surface potential is partly neutralized. This decreases coulombic repulsion between adjacent head groups and allows the formation of larger micelles. A solution having a single, very narrow, distribution of micellar sizes is often called monodisperse.

As concentrations of surfactant or salt (or both) in water are increased, globular micelles gradually turn into larger, rodlike micelles. Under some experimental conditions, spherical and rodlike micelles coexist in the same solution. Systems containing two distinct distributions of micellar sizes are called polydisperse. At higher concentrations of surfactant or salt, rodlike micelles begin to predominate. Finally, at very high surfactant concentrations, lamellar liquid crystal phases may be formed.
Fig. 1.3. Model of hypothetical ionic micelle showing the locations of headgroups, surfactant chains and counterions. Curved arrows symbolize the liquid – hydrocarbon – like nature of the core.
Not all surfactants form micelles in water. Depending on structure, some surfactants disperse in water as lamellar liquid crystal phases or vesicles. The practical result is that water-soluble, single chain surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium bromide, and polyoxyethylene alcohols form micelles in water. Double-chain surfactants such as didodecyldimethylammonium bromide, dihexadecylphosphate, and many phospholipids are insoluble in water and do not form micellar structures.

**Micellization Parameters**

Critical micelle concentration, aggregation number, counterion binding constant, free energy of micellization, etc., are the main micellization parameters. There have been various physico-chemical studies made on micellar solutions for determining these parameters. Among all these micellization parameters cmc is the most significant parameter which has been widely studied and discussed.

**Critical Micelle Concentration:** Many investigators have developed empirical equations relating to cmc to the various structural units in surfactants. Thus, for homologous straight chain ionic surfactants (soaps, alkane sulfonates, alkyl sulfates, alkylammonium chlorides, alkyltrimethylammonium halides) in aqueous medium, a relationship
between the cmc and the number of carbon atoms \( n \) in the hydrophobic chain was found as

\[
\log C_{\text{cmc}} = a - bn \tag{1.1}
\]

where \( a \) is a constant for a particular ionic head at given temperature and \( b \) is a constant \( = 0.3 \) \( (= \log 2) \) at \( 35 \, ^\circ\text{C} \), for the ionic types mentioned above.

The aggregation of monomers to micelles results in a free energy decrease. When micelles are formed, the high energy of the hydrocarbon/water interface is lost, as the chain is now in contact with others of a like nature. Also, the structure of the water around the hydrocarbon part of the monomer is lost. Hence, due to this disorder with respect to water, a positive entropy change and simultaneously a decrease in free energy occurs. Thus, the loss of hydrocarbon/water interfacial energy and loss of water structure are the driving forces for the formation of micelles.

The two most important techniques which are used for determining cmc values are surface tension and solubilization, i.e., the solubility of an otherwise insoluble compound. For an ionic surfactant, the cmc can be obtained easily by conductivity. However as, a very large number of physico-chemical properties are sensitive to surfactant micellization, there are various other techniques, such as self-diffusion measurement, nuclear
magnetic resonance, fluorescence spectroscopy, etc. In case of long–chain surfactants an accurate determination of cmc is straightforward and different techniques give the same results. However, for short–chain, weakly associating surfactants, this is not the case and rather greater care is required not only in the measurements but also in evaluating the cmc from experimental data.

Factors Affecting the Value of Critical Micelle Concentration: When the micelle formation takes place, the properties of solutions of surface-active agents change markedly. Following are the main factors that are found to affect the cmc in aqueous solutions: (i) structure of the surfactant, (ii) the presence of added electrolyte in the solution, (iii) the presence of various organic additives in the solution, (iv) the temperature of the solution, (v) pressure, and (vi) solvents.

(a) Structure of surfactant. In general, the cmc decreases as the hydrophobic character of the surfactant increases, i.e., cmc decreases as the number of the carbon atoms in the hydrophobic group increases (see Eq. 1.1). In aqueous medium ionic surfactants have much higher cmc’s than non-ionic surfactants containing equivalent groups. Zwitterionic surfactants appear to have about the same cmc’s as ionics with the same number of carbon atoms in hydrophobic group. The
cmc increases as the head group is closer to the two branches of the chain partially shielding one another, interfacial energy effects are smallest. In aqueous medium, the cmc’s of ionic surfactants decrease with decrease in the hydrated radius of the counterion.

(b) **Effect of electrolyte addition.** In aqueous solution of ionic surfactant the presence of electrolyte causes a decrease in the cmc. On increasing electrolyte concentration, the forces of electrostatic repulsion between headgroups in a micelle are considerably reduced, enabling micelles to form more easily, i.e., at lower concentration. The order of effectiveness of added electrolytes containing different counterions in decreasing the cmc\textsuperscript{26,27} is {SO}_{4}^{2-} > F^{-} > BrO_3^{-} > Cl^{-} > Br^{-} > NO_3^{-} > I^{-} > CNS^{-} and NH_4^{+} > K^{+} > Na^{+} > Li^{+} > \frac{1}{2} Ca^{2+}.

(c) **Organic additives.** Organic compounds affect the cmc either by penetrating into the micellar region, or by modifying solvent-micelle or solvent-monomer interactions. Non-polar compounds, such as hydrocarbons, that are believed to penetrate into the inner portion of the core, decrease the cmc only slightly. Addition of longer chain alcohols promotes micelle formation and lowers the cmc. The magnitude of cmc decrease depends on the alkyl chain length of the organic additive and the hydrophilic group associated with the chain.
Urea, formamide, and guanidium salts are believed to increase the cmc of surfactants in aqueous solution because of their disruption of the water structure. These water structure breakers may also increase the cmc by increasing the entropy effect accompanying micellization.

Materials that promote water structure (carbohydrates), for similar reasons, decrease the cmc of the surfactant.

(d) **Temperature.** The effect of temperature on micelle formation is essentially guided by the way temperature affects the solubility and other behaviors of surfactants in solution. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes the disruption of the “structured water” surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposite effects, therefore, determines whether the cmc increases or decreases over a particular temperature range.

The thermodynamic parameters (free energy change, enthalpy and entropy) can also be calculated from cmc.

(e) **Pressure.** Many reports have appeared on the effect of pressure on micelle formation of the ionic and nonionic surfactants. With
pressure cmc of ionic surfactants increases up to 1000 atm followed by a decrease above this pressure.\textsuperscript{32-34} Such behavior has been rationalized in terms of solidification of the micellar interior,\textsuperscript{32} increased dielectric constant of water\textsuperscript{35}, and other aspects related to water structure.\textsuperscript{36} For nonionic surfactants, the cmc value increases monotonously and then levels off with increasing pressure.

(f) \textit{Polar nonaqueous solvents}. For micelle formation in polar nonaqueous solvents, the term "solvophobic interaction" has been coined, in analogy with "hydrophobic interactions" which causes micellization in aqueous medium.\textsuperscript{21} The micelles formed due to "solvophobic interactions" are similar in many respects to the micelles that are formed in aqueous medium, although in general, micelle formation is not as favored in nonaqueous solvents as in water for a given surfactant.\textsuperscript{37}

\textbf{Aggregation Number}: The micelle aggregation number \((n_a)\) which is the number of surfactant monomers or dimers making up a micelle, is affected by different factors such as the nature of the surfactant, temperature,\textsuperscript{38} type and concentration of added electrolyte,\textsuperscript{39} organic additives, etc. The value of the aggregation number contains information on the micelle size and shape, which may be important in determining the stability and the practical
applications of the investigated systems. Many methods have been used to determine micelle aggregation numbers like quasi-elastic light scattering, small-angle-neutron scattering, steady-state fluorescence quenching and time-resolved fluorescence quenching.

In aqueous medium, the greater the 'dissimilarity' between surfactant and solvent, the greater the aggregation number. An increase in the temperature appears to cause a decrease in the aggregation number of the ionic surfactants. For non-ionic surfactants, it increases fairly rapidly.

**Structural Transition in Micellar Solutions**

Amphiphilic substances are capable of forming supramolecular systems, from thermotropic-lyotropic liquid crystals and manifold micellar systems up to the highly ordered membranes in liposomes and cells. At low surfactant concentration, first above the cmc, micelles are usually spherical, while at higher concentrations they assume rod- or disk-like shapes. Micelles transform to lyotropic liquid crystalline structures at very high surfactant concentrations.

Not only overall surfactant concentration, but varying other solution conditions such as, surfactant composition, additives in the liquid phase, temperature, pressure, ionic strength and pH are also known to promote structural transition.
The shape of micelles whether they are spherical or rod-like, must be ruled by a balance between the repulsive electrostatic forces of the head groups and the attractive forces that cause the aggregation. It thus seems reasonable that the shape transition points depend on the head group including the counterion as well as the chain length of the surfactant and the location of the solubilizate in the micelles.

The shape and size of these micellar aggregates can, in principle, be determined by various methods, such as viscosity,\textsuperscript{52} small-angle-neutron scattering (SANS),\textsuperscript{53} light scattering,\textsuperscript{54-56} ultrasonic absorption\textsuperscript{57}, time-resolved fluorescence,\textsuperscript{58,59} etc.

Growth of the aggregates has been observed by light scattering,\textsuperscript{60-63} viscosity,\textsuperscript{64-68} flow birefringence measurements,\textsuperscript{69} SANS,\textsuperscript{70-72} and by Cryo-TEM.\textsuperscript{73,74}

**Packing Parameter:** The shape of micelles depends strongly upon the actual packing parameters in micellar assembly.\textsuperscript{75-77} The surfactant packing parameter, introduced by by Israelachvili et al.\textsuperscript{78} provides an empirical criterion for predicting the shape that the aggregates of a given surfactant will adopt in aqueous solutions. The packing parameter, $R_p$, is given by: $R_p = v/a.l$ where $v$ is the volume occupied by the hydrophobic moiety of the amphiphilic molecule, $l$ is the critical length in the fully extended
conformation and \( a \) is the optimal cross section surface area occupied by an amphiphilic headgroup at the water-aggregate interface. Both \( l \) and \( v \) can be calculated for a saturated hydrocarbon chain of \( n \) carbon atoms using Tanford's equations:

\[
l = (1.5 + 1.265 n) \text{Å}, \tag{1.2}
\]

\[
v = (27.4 + 26.9n) \text{Å}^3, \tag{1.3}
\]

Specific values of \( R_p \) are associated with spherical micelles \((R_p < 0.33)\), worm-like micelles \((0.33 < R_p < 1)\), flat bilayers \((R_p = 1)\), and inverted micelles \((R_p > 1)\). The factors that influence the mobility of the hydrophobic chains and the hydration of the headgroup, e.g., unsaturation in the hydrophobic tail, pH, temperature and the presence of the electrolytes may affect the \( R_p \)-value.

**Effect of Additives on Growth Process:**

**(a) Effect of salts.** For concentrated surfactant solutions, the inorganic salts are used as thickening agents. The effects of inorganic salts on ionic surfactant solutions have been discussed in terms of electrostatic interactions, changes in the structure of water, ionic hydratability, etc.\(^{77,80-83}\)

The repulsive force between the head groups is decreased by the presence of salt ions near the polar heads of the surfactant molecules. Due to this reduction in the repulsion, the surfactant molecules approach each other
more closely and as a result larger aggregates are formed which require much more space for the hydrophobic chains. The two main factors which are responsible for structural transition in presence of salts are – (a) electrostatic effect of simple salts due to the counterion binding on ionic micelles, (b) hydrophobic interaction between surfactant molecules or ions caused by the change in the hydrogen–bonded structure of water. It has been reported that the micellar sphere-to-rod transition is highly dependent upon the nature of the counterions. The micellar transition is promoted by the strong counterion binding, which can be shown by higher increase in the relative viscosities.\textsuperscript{67,69,84-92} The salt-induced formation of rod-like micelles in aqueous salt solutions has been reported for a series of cationic surfactants\textsuperscript{63,93-105} by different techniques such as light scattering,\textsuperscript{95,97,102} flow birefringence,\textsuperscript{101,103} viscosity,\textsuperscript{95} solubilization,\textsuperscript{96,100} \textsuperscript{1}H NMR,\textsuperscript{98} SANS,\textsuperscript{99,105} and electron microscopy.\textsuperscript{104}

Counterions are ‘bound’ primarily by the strong electrical field created by the head groups but also by specific interactions that depend upon head groups and counterion type. Micellar shapes should be determined under experimental conditions because the shape of the micelles are sensitive to surfactant chain-length, structure of the head group and type of the counterion.\textsuperscript{1,20,106-108}
Specific counterion effects on a variety of micellar shapes generally follow a Hofmeister series, i.e., for counterions of the same valence, the size of the micelle increases with size of the counterion (crystal radius) and the ease of dehydration of counterion. However, sphericity may also depend upon the interactions of hydrogen bonding between hydrated counterions and head groups and counterions, and the possibility that a fraction of the counterions are sitebound to surfactant headgroup, e.g., contact ion-pair formation cannot be ignored.

Double tailed amphiphiles usually form bilayer sheets, as their most hydrated state allows the molecules to pack only in a lamellar arrangement. When bilayer sheets are closed, vesicles are formed. Lamellar aggregates are also formed from the mixtures of anionic and cationic surfactants in water or mixtures of ionic surfactants and long-chain alcohols in water or electrolyte solution. Some surfactant molecules in aqueous solution are spontaneously transformed from micelles into a lamellar array in the presence of a high salt concentration. This morphological change is facilitated by an increase in counterion binding and dehydration of the surfactant head groups and bound counterions. This salt-induced lamellar arrangement of surfactant molecules is commercially utilized in liquid laundry detergents.
(b) *Effect of organic additives.* The effect of organic additives on the micellar size and shape has been explained in terms of their effects on water structure and on their role inside the micelle. Aqueous micellar solutions are known to solubilize water insoluble or slightly soluble organic compounds. It has been suggested that the short chain alcohols are localized mainly in the aqueous phase, which therefore changes 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 localized in the micellar phase.\textsuperscript{123,124}

At the air-water interface,\textsuperscript{125} amines are more surface active than alcohols. Due to electrostatic and hydrophobic effects, C\textsubscript{4}-C\textsubscript{10} \textit{n}-alkyl amines are solubilized in micelles and the amine group is left at the micellar surface.\textsuperscript{126}

On the basis of their hydrophilicity three different classes of additives were ranked by Wormuth et al.\textsuperscript{127} Primary amines were found more hydrophilic than either alcohols or carboxylic acids. But when coupled with anionic surfactant the hydrophilicity of amine was lower than expected. On comparison, amines have been found to be more effective in SDS than in TTAB as observed by Lindemuth and Betrand.\textsuperscript{128} This is due to the interaction between the amines and the anionic surfactant headgroup at the
micellar interface. Besides this, amine head group has the ability to reside deeper in the SDS micelle, which relieves the requirement of the tails of the surfactant to reach the center of the micelle at a shorter alkyl chain length of additive. In case of interaction of cationic surfactants with carboxylic acids similar effects were seen. Thus, a cosurfactant with the ability to bear an opposite charge to that of the surfactant headgroup, is more effective at promoting sphere-to-rod transition and has the ability to better penetrate the surfactant rich film, separating the micellar and aqueous pseudophases. 

Similar effect was seen by Prasad and Singh in case of SDS and CTAB micelles.

It is well known that to maintain a spherical form, the micellar tails must be reachable to the center of the micelle. On addition, an aliphatic hydrocarbon generally resides in the micellar core. Now the association structure can maintain spherical form containing the solubilized oil at a radius which was previously prohibitive. In this way the presence of aliphatic hydrocarbons retard the structural transition.

On the other hand, the presence of aromatic hydrocarbons stimulate rod growth in case of cationic surfactants, which may rise from the interaction of the delocalized \( \pi \)-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 transition to rods by shrinking the surface area occupied per amphiphile, thus increasing the aggregation number.

(c) **Synergistic effect of salts + organics.** Kabir-ud-Din and coworkers\textsuperscript{131-137} reported that the combined presence of salts and organic additives produces a synergistic effect (e.g., significant increase in viscosity) in micellar solutions. This synergism is dependent on the nature of the additives. It was also found that the presence of salt may change the conventional solubilization site of a particular additive and thus produce different micellar morphologies.

The effect of addition of \textit{n}-alcohols on the viscosity of CTAB\textsuperscript{138} was studied by capillary viscometry method. Prasad and Singh 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 concentration were found to increase the viscosities. Depending on the nature of the alcohol, further addition made the solution either turbid or lowered the viscosity of the solution. The result was interpreted in terms of the possible micellar transition from rod to sphere or elongated rods in presence of added alcohols. It is known that rod-shaped micelles are formed in aqueous solutions of 0.1M CTAB + 0.1 M KBr.\textsuperscript{139} The effects of added
aliphatic \( n \)-amines (C\( _4 \), C\( _6 \), C\( _7 \) or C\( _8 \)NH\(_2 \)) and temperature on the above system show that transition of rod-shaped micelles to larger aggregates is induced by addition of higher amines (>C\( _6 \)NH\(_2 \)) and that too unto a certain concentration only: a further increase in concentration produced the opposite effect. Addition of C\( _4 \)NH\(_2 \) amine was reported to induce only a rod-to-sphere transition. Kumar et al.\(^{140} \) interpreted the data in terms of solubilization/incorporation (decrease of micellar surface charge density) of amines inside in the micelles and nature of the effective solvent (water + amine). The latter effect dominated the change from larger aggregates to smaller micelles at higher concentrations of the added amine.

**Micellar catalysis**

Most important reactions occur not in a homogenous solution but at an interface. Many industrially important processes occur on the surfaces of solid catalysts, and nearly all biological reactions take place at gas-liquid interfaces or on an enzyme that may itself be bound to a membrane. The properties of these catalytic surfaces depend critically on the detailed structure of the surface, which can be controlled by adding agents that may themselves take no direct part in the chemical reactions.\(^{141} \)

The above lines are applicable to micelle-catalyzed reactions. A solution containing micellar aggregates is macroscopically homogeneous
(i.e., is one phase). However, microscopically this phase is separated into many small regions of high solute concentration (micelles) dispersed in a solvent region. Any reactive species added to the solution distributes itself between these regions. If the conditions in these two environments result in different reaction rates, then the micelles act as either catalysts or inhibitors.\textsuperscript{142} The catalytic efficiency is governed both by the affinity of the reagents for the micelles and by the reactivity of the bound reagent molecules.

Surfactant micelles provide a unique microenvironment for the compounds when they are solubilized in an aqueous solution. Surfactant micelles are able to provide either a polar region or a region of high charge density, accompanied by an electrostatic potential of up to a few hundred millivolts at the micellar surface, and a nonpolar hydrophobic region in the micellar core. Micelle aggregation numbers usually range from less than 100 for ionic surfactants to several hundred for nonionic surfactants. Therefore, the kinetics of micellar solutions is governed by electrostatic and hydrophobic interactions between micelles and reactants, transition complexes, and products. It is logical, therefore, that a combination of hydrophobic and electrostatic interactions result in the orientation and concentration of polar or charged compounds in ways that are not possible in
simple solutions in organic solvents. If any of the reaction species interacts with micelles, then the presence of micelles affect the reaction rate.

The observed rate of a chemical reaction ($R_\psi$) in micellar solutions is considered to be the sum of the rates in the continuous aqueous phase ($R_w$) and micellar pseudophase ($R_m$).\textsuperscript{22,23}

$$R_\psi = R_w + R_m$$  \hspace{1cm} (1.4)

Thus, for a bimolecular reaction between A and B in aqueous micelles:

$$k_\psi [A][B] = k_w [A]_w [B]_w + k_m [A]_m [B]_m$$ \hspace{1cm} (1.5)

where observed rate constant $k_\psi$ is found on the basis of the moles of A and B in the total volume of the system, $V_t$. Subscript w refers to the water phase and subscript m to the micellar phase. In the simplest case, both reactants are entirely bound to the micelles and the reaction takes place completely in the micellar phase. The rate of reaction in water can be neglected, so that the first term on the right hand side of Eq. 1.5 is negligible. This leads to the expression:

$$k_\psi = k_m [A]_m [B]_m / [A][B]$$ \hspace{1cm} (1.6)

For this special case of totally bound reactants $[A]_m = [A] / \phi_m$ and $[B]_m = [B] / \phi_m$, where $\phi_m$ is the volume fraction of the micellar phase. Using these relations in Eq. 1.6 gives:

$$k_\psi = k_m / \phi_m^2$$ \hspace{1cm} (1.7)
Eq. 1.7 shows that the observed rate is enhanced by compartmentalization of reactants into the reaction volume $V_t \phi_m$, producing an apparent catalysis. Rate enhancement is mainly a consequence of high reactant concentrations in the micellar volume, which contains all the reactants. Eqs. 1.5 and 1.6 can also explain kinetic control of selectivity of catalytic reactions in micelles. If the two reactants are spatially separated in micellar and water phases by virtue of their solubility properties, the rate of reaction is decreased compared to the case where both reactants are present only in the micellar phase.

Ninhydrin $\alpha$-isoleucine reaction has been used as prototype to investigate the catalytic activity of gemini surfactants.

**Importance of the Research Problem**

“Gemini surfactants” have structures and properties, which are different from those of monomeric surfactants and are said to be “unique to the world of surfactants”. These surfactants show high surface activity, unusual viscosity changes with an increase in [surfactant], a low critical micelle concentration (cmc), and unusual micellar structures. Geminis have already been utilized in many fields as in skin care, antibacterial regimens, construction of high porosity materials, analytical separation and solubilization process.$^{13-17}$
Survey of available literature reveals that no serious attempt has been made to study the micellization phenomenon of gemini surfactants in polar non-aqueous solvents. The micellization tendency of the surfactants decrease in presence of organic solvents. Detailed study showed that the gemini nearly outclass the micellization arresting property of solvents. The implications of the results obtained of gemini micellization in polar-nonaqueous solvents may be useful in micellar catalysis.

A vast majority of experimental data are available on solution/aggregational behavior of conventional surfactants in presence of different classes of additives. Most studies on geminis also are related to their specific aggregation behavior and structural properties\textsuperscript{143-145} but morphological studies of geminis in the presence of different class of additives has not been systematically investigated. Being an entirely a new field of research, additive effects were studied by viscometry and DLS techniques. From a practical point of view, the presence of non-spherical micelles gives solution a very high viscosity which might be of importance in industrial formulations as it may enhance performance and customer appeal of formulation.

The use of ninhydrin for the detection and estimation of amino acids has been the subject of various investigations because of its potential ability
to reveal latent fingerprints. The use depends on the formation of a purple-colored product (*Ruhemann's purple*) whose amount depends upon reaction conditions, i.e., pH, temperature, reactant concentrations, etc. The technique, although useful, still has room for improvements. With the view that the method could find applications to improve contrast and visualization of ninhydrin-developed fingerprints and may prove a step forward from the methods already used in current forensic research, systematic kinetic studies were performed of the ninhydrin-L-isoleucine reaction in the presence of micellar media. Due to improved performance of geminis on almost all fronts for which conventional surfactants are utilized, effects of three synthesized geminis on the rate of ninhydrin-L-isoleucine reaction were studied in detail. Optimum conditions can be obtained by studying the effect of various factors on the rate and extent of the reaction. The reaction rates are enhanced as compared to conventional surfactants.
The Lay – Out of the Thesis

Chapter-I. General Introduction.

Chapter-II. Experimental

Chapter-III. Micellization phenomenon of gemini surfactants in polar nonaqueous-water mixed solvents.

Chapter-IV. Viscometric and DLS studies on aqueous gemini surfactants in presence of additives.

Chapter-V. Catalytic activity of gemini surfactants and effect of organic solvents on the ninhydrin-L-isoleucine reaction.
References


