Summary
“Surfactants”, a happy and convenient contraction of “surface active agents”, owe their name to their interesting behavior at surfaces and interfaces. 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. 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.

Among the major incidences that happened in the world of surfactants, the most interesting is the outburst of researches on ‘gemini surfactants’. "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. 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 head groups in the gemini surfactants also influences their aggregation properties.

A well defined, but not abrupt, change in physical properties of surfactant solutions as one passes from a threshold value of [surfactant] is known as critical micelle concentration (cmc). Near the cmc, micelles are usually spherical and the radius of the micelle is nearly equal to the length of the surfactant molecule. Upon continuous increase of concentration of the surfactant, spherical micelles become rod-shaped and subsequently these rods become hexagonally packed structures.

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 availability of organic additives also suppresses headgroup repulsion and promotes sphere-to-rod transition in micellar structures.\textsuperscript{12}

Micellar solutions are known to affect the rates of chemical reactions and the positions of chemical equilibria.\textsuperscript{13} It is generally accepted that ionic reactions occur at the micellar surface adjacent to the head groups. Rate enhancements of biomolecular reactions by aqueous micelles, or similar colloidal assemblies, are due largely to bringing together of both reactants in the small volume of the micelles. The hydrophobic and electrostatic factors play an important role in the micellar catalysis. Out of these two factors, hydrophobic effect is the most important in the organization of the constituent molecules of the living matter into complexes.

Keeping in view the importance of the novel type of surfactants, the geminis, the present thesis delves into such topics as critical micelle concentration, aggregate size and shape, and catalytic role of geminis towards ninhydrin-amino acid reactions. There are five chapters in the thesis:
In the **General Introduction (Chapter-I)**, a detailed account of the behavior of surfactants, their classification, micellization, factors affecting cmc, structural transition, effect of additives on growth process and micellar catalysis are described. The importance of the research problem and an up-to-date literature survey related to the work described in subsequent chapters are also included.

**Chapter-II** contains the experimental details of the work. A list of chemicals used in the investigation is also included in this chapter. The main methodologies adopted are: conductance measurements, viscometric measurements, pH- measurements, dynamic light scattering measurements (DLS), spectrophotometric measurements and $^1$H NMR measurements.

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. In **Chapter-III**, studies on the micellar properties [cmc, degree of counter ion dissociation ($\alpha$), and thermodynamic parameters ($\Delta G^o_m$, $\Delta H^o_m$, and $\Delta S^o_m$)] of the gemini surfactants, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_s-\text{N}^+(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}, 2\text{Br}^-$ ($s = 4, 5$ or $6$; $16-s-16$) in water and polar nonaqueous solvent (1-propanol, PrOH; 2-methoxyethanol or methyl cellosolve, MC; dimethylsulfoxide, DMSO; acetonitrile, AN) –
water mixtures are reported. Conductometry was used to determine the cmc and \( \alpha \)-values. The micellization of gemini surfactants occurs in many adverse situations, such as in the presence of nonaqueous solvents which are known to arrest the phenomenon of micellization. Therefore, these systems may be utilized for the organic reactions which are occurring in polar solvents or in the presence of binary solvents whose one component is water.

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 are related to their specific aggregation behavior and structural properties\(^\text{14-16}\) 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, viscometric and dynamic light scattering (DLS) measurements have been performed on the dimeric gemini surfactants to see the role of organic additives (alcohols; \( \text{C}_4\text{-C}_6\text{OH} \) and hexylamine; \( \text{C}_6\text{NH}_2 \)) in the absence and presence of KBr towards micellar growth. With respect to the corresponding monomeric surfactant cetyltrimethylammonium bromide (CTAB), dimeric surfactants have been found to have a much stronger tendency for micellar growth. The results are described in Chapter-IV. The addition of a general ionic salt KBr plays a role in weakening electrostatic repulsions between the
gemini micelle cationic headgroups and thereby induces structural changes from spherical to rod-like or disk-like shape. The presence of primary alcohols (butanol, pentanol, hexanol) enhances the sphere-to-rod transition and reduces the threshold concentration for the onset. This is due to the formation of the gemini-alcohol mixed micelles. Thus, the micellar size is larger in presence of alcohols as confirmed by the applied techniques. The alcohols progressively get embedded between the monomers of the micelle, which increases the volume of the micellar core. Thus, longer alkyl chain alcohols form efficiently larger micelles. A combined presence of KBr and alcohols or n-hexylamine shows a synergistic effect, which produce favorable conditions for micellar growth which do not exist in presence of either the salt or additive alone. For additives of equal chain length of alcohol and amine (C₆OH and C₆NH₂), the alcohol is found more effective for cationic gemini micellar growth.

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 (pH, [L-isoleucine], [ninhydrin], solvents) on the rate and extent of the reaction. The following conclusions are made regarding the catalytic effect of the gemini micelles (16-s-16, s = 4, 5, 6) on the ninhydrin L-isoleucine reaction, investigated at pH = 5 and 80 °C: Dicationic gemini micelles provide much better environment for ninhydrin-L-isoleucine reaction as compared to their corresponding monocationic counterpart CTAB micelles. It is known that the spacer chain at headgroup level of geminis decrease the extent of water penetration at the micellar surface: this could be the reason of kinetic advantages of the geminis used in the present studies. In addition to typical rate constant increase and leveling-off regions (just like conventional CTAB), an unusual third region of increasing $k_w$ at $[16-s-16] \geq 60 \times \text{cmc}$ was observed. $^1$H NMR studies reveal the formation of
larger aggregates at these higher surfactant concentrations which provide less polar environment and hence $k_v$ increases. Based on the above, the ninhydrin-L-isoleucine reaction can thus be used as a simple and reliable kinetic probe in aggregate structures. The catalyzing effect of organic solvents (1-propanol, methyl cellosolve, acetonitrile, dimethylsulfoxide) seems due to the blockage of side reaction(s) and higher solubility of the product.
References


