

# Chapter VI

## Summary and Conclusion

In summary, the thesis embodies the results of the physico-chemical studies on selected amphiphiles and their aggregation behaviour in different media. The amphiphiles were selected, so as to form the different types of aggregates, viz; micelles, wormlike micelles and vesicles in solution. Ammoniumdodecyl sulphate (ADS) forms micelles alone in aqueous solution and also in presence of aqueous electrolytic media of tetraalkylammonium bromides (TAAB), cetyltrimethylammonium bromide (CTAB) forms micelles in aqueous solution above the cmc and the same solution forms highly viscoelastic wormlike micelles in a medium where hydroxyaromatic dopants are present. On the other hand, dimethyldioctadecylammonium bromide (DDOAB) forms vesicles in aqueous solution at low surfactant concentrations above a critical temperature known as the gel-to-liquid crystalline phase transition temperature ( $T_m$ ). Present studies are carried out in different electrolytic media (e.g, TAA<sup>+</sup> ions), at various pH and also in vesicular media. A chapter wise summaries and the conclusions drawn from the experimental works are summarised below. The references have been cited at the end of each chapter.

The first chapter [**Chapter I. Surfactant Aggregation in Solution: An Overview**] describes the general information on the subject dealt in the thesis. An overview of the different types of aggregates formed, viz., micelles, wormlike micelles and vesicles, as a result of self-assembly of amphiphilic molecules in solution is given. The morphology sequence and phase behaviour of surfactant aggregates is driven by the spontaneous curvature of the hydrophobic/hydrophilic interface and may be tuned by various external factors, such as the amount and nature of added electrolyte, the presence of other species in solution, the pH or the temperature. Since, the type of aggregates (of surfactants in solution) at a certain concentration depends on the intrinsic surfactant geometry, which can be understood on the basis of the critical packing parameter (CPP), a brief description on the CPP is also

outlined. Considering the importance of amphiphiles in chemistry, biology and in industry and their wide range of applications, the chapter concludes with descriptions on the practical applications of amphiphilic assemblies in solution.

The second chapter [Chapter II. Scope and Object] of the thesis describes the scope as well as the object of the present study.

In the third chapter [Chapter III. Studies on the Aggregation Behaviour of Ammoniumdodecyl Sulfate in Presence of Symmetrical Tetraalkylammonium Salts] the physico-chemical studies on the micellization of ADS in water and in different tetraalkylammonium bromides viz, tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrapropylammonium bromide (TPAB) and tetrabutylammonium bromide (TBAB) have been carried out. Micellization, which is a manifestation of hydrophobic effect, is likely to undergo a significant change in the presence of such additives. The critical micellisation concentration (cmc) of ammoniumdodecyl sulfate (ADS) in different tetraalkylammonium bromides in the salt concentration range of 0.0005-0.005M were measured by electrical conductivity method. Substantial decrease in the cmc of ADS with increasing concentration of each of the above mentioned electrolytes were observed. This can be accounted for by the fact that in solutions of high ionic strength, the forces of electrostatic repulsion between the surfactant head groups in a micelle are considerably reduced due to charge screening. The charge screening increases the attractive force operating in the vicinity of the micellar head and the positive counterion of the electrolyte making the so-called palisade array more densely packed, thus promoting micelle formation to be more favorable. It was found that micelle formation of ADS in these electrolyte media of progressively larger tetraalkylammonium bromides favors cmc lowering in the order TBAB > TPAB > TEAB > TMAB.

TMA<sup>+</sup> ions with smallest ionic size are most hydrated in aqueous solution among all the ions in the group. Therefore, the hydration shell of TMA<sup>+</sup> ions limits the distance of closest approach to the micellar heads of ADS, causing a small reduction in cmc as compared to TEA<sup>+</sup>, TPA<sup>+</sup> or TBA<sup>+</sup> ions. In other words it appears that this salt behaves as the common non-hydrophobic electrolytes,

interacting only with the ADS micelle surface (stern layer) and screening the ionic charge around that location. The other ions have short hydrocarbon chains and some of these chains are supposed to penetrate in the micellar core due to hydrophobic interaction. Hence, at a given temperature, micelle formation of ADS in these electrolyte media favours a cmc lowering in the above mentioned order. Therefore, the lowering in cmc is due to the ability of the TAA<sup>+</sup> ions to interact electrostatically as well as hydrophobically with the micelles of ADS. The degree of counterion binding ( $\beta$ ), evaluated using the Corrin-Harkins relation, is largest for TBAB and smallest for TMAB.

The thermodynamic functions of micellization,  $\Delta G_{mic}^{\circ}$ ,  $\Delta H_{mic}^{\circ}$  and  $\Delta S_{mic}^{\circ}$ , were evaluated in 0.001M of different TAAB solutions in the temperature range of 288.15-318.15K.  $\Delta G_{mic}^{\circ}$  was always found to be negative and shifts to more negative values with increasing size and hydrophobicity of the counterion of the added electrolytes. In the investigated temperature range of 288.15 to 318.15K, large positive  $\Delta S_{mic}^{\circ}$  values suggest the overall micellization to be entropy driven. Like a variety of processes such as oxidation-reduction, hydrolysis, protein unfolding, etc., micellization too was found to exhibit a linear relationship between the enthalpy and entropy, generally known as enthalpy-entropy compensation. The small variation of  $\Delta G_{mic}^{\circ}$  with temperature is reflected in a good correlation between the enthalpy and the entropy for the present system.  $\Delta H_{mic}^{\circ}$  and  $\Delta S_{mic}^{\circ}$  was found to compensate each other with compensation temperature of  $304 \pm 2K$ .

Aqueous ADS neither display clouding alone nor in presence of TMAB, TEAB, or TPAB salts. However, the same surfactant solution shows clouding (at the cloud point, CP) in presence of TBAB salt. The phenomenon of clouding is studied at fixed concentration of ADS and varying concentrations of TBAB and also at fixed TBAB concentration and varying concentrations of ADS. At fixed concentration of TBAB, the CP increases with the increase of ADS, while it is decreased with an increase in TBAB concentration at constant concentration of ADS. The increase in the CP with increasing [ADS] at a fixed [TBAB] is due to the increased electrical repulsion between the micellar surface head groups caused by the decrease in effective salt content per micelle. On the other hand the decrease in

CP with increasing TBAB can be accounted for in terms of hydrophobic interaction and surfactant head group dehydration. The butyl chains of TBAB are supposed to be embedded between the monomers of the of ADS micelles through hydrophobic interaction. Increase in the temperature at this point causes dehydration of the anionic heads of the ADS micelle that in turn leads to a greater electrostatic attraction between the anionic heads and TBA<sup>+</sup> counterions. Further increase in the [TBAB] causes more structured water to be replaced by the butyl chains and this causes the aggregates to be removed from aqueous phase at low temperature.

The most important result of the present investigation is the fact that CP decreases steeply at the initial [TBAB], but changes little above the [TBAB]/[ADS] mole ratio of 1:1. Upto the [TBAB]/[ADS] mole ratio of 1:1, TBA<sup>+</sup> ions interact with ADS micelles both hydrophobically as well as electrostatically and replace weakly interacting ammonium ions from the micelles. Therefore, the manifestation of the effect of TBA<sup>+</sup> in decreasing the CP is very high initially. Above the composition of 1:1, the interaction of TBA<sup>+</sup> with the surfactant micelles is apparently very weak. In addition to the above it was also found that slightly less than one mole of TBAB per two moles of ADS is required for clouding to occur.

In the fourth chapter [**Chapter IV. Studies on Microstructural Transition of Micellar Aggregates in Presence of Hydroxyaromatic Dopants: Rheology and Spectroscopy**] the effect of neutral hydroxyaromatic compounds on the microstructural transition of CTAB micelles, from spherical to wormlike micelles and then to vesicles, are studied. Micellar aggregates that can grow anisotropically under appropriate conditions, changing their shapes from spheres to rods or highly flexible wormlike aggregates, provide some analogies between giant flexible cylindrical micelles and conventional polymeric solutions. The polymerlike micelles (wormlike micelles) which are formed by certain ionic surfactants in solution exhibit very interesting rheological properties. At high concentrations, these solutions show typical viscoelastic behaviour while at very low concentrations more complex and unusual rheological phenomena is observed. Stimuli-responsive properties of viscoelastic gels of long wormlike micelles are fascinating and have created a great deal of interest in recent years.

The most extensively studied system in respect of viscoelastic gel formation is the cetyltrimethylammonium bromide (CTAB) micelles in presence of a hydrotrope, sodium salicylate. The presence of an anionic charge on the promoter molecule has been considered pivotal in achieving low concentration shape transition of cationic micelles via charge screening because it decreases the average area per surfactant head group allowing the packing parameter to exceed the critical value of  $\frac{1}{2}$ . However, other important factors including the role of OH group of the promoter molecule have not attracted much attention, and as such, the puzzling question as to why not only its presence but also its position in the aromatic ring of NaSal molecule is so vital remains broadly unanswered. Therefore, to understand the role of the OH group precisely, it was tempting to check what would happen if uncharged naphthols with strong hydrophobic part (and no anionic charge) is used. In this chapter the result of the investigation of the effect of neutral 1- and 2-naphthols and also the dihydroxy derivatives, 2,3- dihydroxynaphthalene (2,3-DHN) and 2,7-dihydroxynaphthalene (2,7-DHN), on the shape transition of CTAB micelles is recorded. The result shows that intermolecular H bonding between OH groups of micelle embedded naphthol molecules plays a key role in micellar shape transition in absence of any charge screening of head groups and imparts strong viscoelasticity to the dilute aqueous surfactant solution. The viscosity of the systems comprising of CTAB and the hydroxyaromatic dopants are maximum at the surfactant to dopant mole ratio of 1:1. Therefore, the shear induced rheological studies were carried out at a mole ratio of 1:1.

To understand the exact role of hydrogen bonding in the above mentioned shape transition, studies with methoxynaphthalenes were also carried out under similar conditions. The methoxynaphthalene-CTAB systems (1-methoxynaphthalene/CTAB and 2-methoxynaphthalene/CTAB), neither display the ability to develop viscoelasticity in the system nor exhibit any viscosity modification with applied shear, and behave completely like a Newtonian liquid. This result is quite surprising in view of the fact that much like 1- and 2-naphthols, both 1- and 2-methoxynaphthalenes are embeded into the micelles of CTAB. Though methoxynaphthalenes possess a similar structure and hydrophobicity to that of hydroxynaphthalene molecules but because the methoxynaphthalenes

cannot act as hydrogen bond donors, they fail to promote the micellar shape transition and to impart viscoelasticity to the CTAB solution.

The effect of temperature and pH on the shear induced viscoelasticity of the systems showed interesting results. With increasing temperature the viscosity of the system increased upto a critical temperature of  $\sim 26^{\circ}\text{C}$  and then decreased. As the temperature was increased, naphthol molecules (uncharged) becomes more soluble and gets partitioned more strongly in the micellar phase. This favors the formation of longer wormlike micelles up to the critical temperature, above this temperature the increased kinetic energy allows the surfactant unimers to hop more frequently between the body and the end cap resulting in the breaking up of the wormlike micelles, thus decreasing the effective viscosity. The motivation behind carrying out the study at different pH stems from the fact that the hydroxyaromatic dopants which, under neutral conditions activate the formation of worm-like micelles at pH  $\sim 5.0$  may, on partial ionization of the OH group, increase the packing parameter further via charge screening. This in turn could pave the way of designing a route for pH-responsive vesicle formation. As expected the systems showed a transition of morphology from highly viscous wormlike micelles to less viscous globular vesicles at higher pH. The results were further confirmed by cryo-TEM images.

To understand the kind of interactions which are operative in the micelle-dopant systems, spectroscopic studies are also carried out. The spectral characteristics of naphthols (which contain OH) were compared with those of methoxynaphthalenes (which do not contain OH) under various conditions in order to visualize a consistent molecular picture. The location and orientation of the additive molecules in the micelles were ascertained by  $^1\text{H}$  NMR studies. The signals from the aromatic ring protons of the naphthol molecules were shifted upfield when  $\text{D}_2\text{O}$  solutions of CTAB and naphthols were mixed in 1:1 mole ratio. The  $\text{CH}_3$  protons of CTAB head group and the adjacent  $\text{CH}_2$  protons, which resonate at 3.132 and 3.289, respectively, in  $\text{D}_2\text{O}$ , were shifted upfield and were found to resonate at 2.746 and 2.397, respectively, in the presence of naphthol. However,  $\text{CH}_2$  protons adjacent to CTAB head group, were affected the most in presence of naphthols, and unlike pure CTAB, the signal from  $\text{CH}_2$  protons

emerged on the other side of CH<sub>3</sub> protons of CTAB head groups. From the above observation it was concluded that the solubilized naphthol molecules were penetrated not deep inside the micellar core but were present near the surface probably with a well-defined orientation in which the OH groups are protruded from the micellar surface toward the polar aqueous phase. The degree of upfield shift of the signals from methoxynaphthalenes (in CTAB micelles) were less than those of the naphthols, indicating a stronger partitioning of the naphthols in the micelles.

The possibility of hydrogen bonding and  $\pi$ - $\pi$  interaction in naphthols have been checked by observing the effect of CTAB micelles on the absorption spectrum of the hydroxyaromatic compounds. UV absorption spectra of the dopants (probes) were modified in their ground electronic state showing significant red-shifting and presence of isobestic points. The modifications are explained in terms of the formation of hydrogen bonding network between the micelle embedded naphthol molecules and the interfacial water molecules. The relatively less polar and less mobile water molecules compared to bulk water forms strong H-bond with the OH group of embedded naphthols, which act as H-donors and results in an optimum orientation of aromatic  $\pi$ -electron systems in the micelles to shield the surfactant headgroup charges efficiently; maybe via cation- $\pi$  interaction; i.e., the cation charge of surfactant head groups interacts with the quadrupole moment of the aromatic  $\pi$ -system of naphthols. The methoxynaphthalenes on the other hand showed very little shift and no isobestic point could be observed. In methoxynaphthalenes the ability of intermolecular H-bond formation disappears and therefore, the small red-shift, with the absence of any isobestic point(s), compared to that in naphthols indicates that a weaker noncovalent interaction takes place. The chapter concludes with the cryo-TEM investigations, which definitely proves the existence of wormlike micelles at ordinary pH and vesicles at high pH value.

In the fifth chapter [**Chapter V: Studies on Vesicular Aggregates of Dimethyldioctadecylammonium Bromide (DDOAB): Influence of cosurfactant and Hydroxyaromatic Dopants**] the effect of cosurfactants and hydroxyaromatic dopants on vesicular dispersion of aqueous dimethyldioctadecylammonium

bromide (DDOAB) have been investigated. In aqueous solution the amphiphile DDOAB forms vesicles which have close relationship with biologically important structures formed by phospholipids. At low temperatures the di-alkyl chains pack in an ordered fashion but with increase in temperature the vesicle is found to undergo a gel-to-liquid crystalline phase transition at a temperature  $T_m$ , characteristic of the system. Addition of solutes viz., single chain surfactants or hydroxyaromatic compounds viz., 1- and 2-naphthols and dihydroxyaromatic compounds viz., 2,3-dihydroxynaphthalene and 2,7-dihydroxynaphthalene to aqueous dispersion of DDOAB changed the phase transition temperature as well as other parameters characteristic of the vesicle.

The chapter comprise mainly of three parts. In section 5.4 of this chapter the interactions of micelle forming nonionic surfactant, Polyoxyethylene Sorbitan Monolaurate (Tween 20), with spontaneously formed vesicles of DDOAB have been investigated by Differential Scanning Calorimetry (DSC), Turbidity, Dynamic Light Scattering (DLS) and Fluorescence Anisotropy measurements. The DSC thermogram of pure aqueous DDOAB dispersion showed two endothermic peaks at 36 °C and 45.2°C. The peak at 45.2°C has been identified as the main gel-to-liquid crystalline phase transition temperature and the one at 36°C has been assigned to the melting of the patches perturbed by the vesicle-vesicle interaction/aggregation. Addition of small fraction of Tween 20 (0.1 molar ratio) in aqueous DDOAB replaces the two extrema at 36°C and 45.2°C with a single transition peak at 44.4 °C. Further increase in the above molar ratio leads to lower  $T_m$  and more broadening of the gel-to-liquid crystalline phase transition temperature peak was observed. The broadening of the transition peak indicates that a two-phase gel to liquid crystalline region is crossed with each phase making a contribution to the enthalpy change. This region most probably corresponds to the region where micelles and vesicles coexist. At still higher mole ratio the peak flattens and ultimately disappear at around Tween 20/DDOAB ~ 4, indicating complete solubilisation of DDOAB vesicle dispersion.

Turbidity data reveals that the vesicle-to-micelle (V-M) transition takes place in three stages: at first, the vesicle bilayer is saturated with Tween 20; followed by mixed micelles formation and finally a complete solubilisation of the

vesicle. DLS measurements have shown that the increase in the turbidity of the solution was due to an increase in the mean size of the vesicle from ~324 to ~353 nm as a result of incorporation of Tween 20 into the bilayer. To explore the changes induced by Tween 20 on the rigidity of the molecular environment of the vesicle bilayer, fluorescence anisotropy of DPH molecule in DDOAB dispersion were also studied. The fluorescence anisotropy values of the probe molecule for the lowest Tween 20/DDOAB molar ratio of 0.02 is much higher (~0.218), as expected for lipids in a more ordered gel state below the  $T_m$ . The value remains almost steady upto molar ratio of 0.20, showing the restricted movement of the bulky DPH probe within the solid-like chain environment of the vesicle bilayer. However, once the disruption of the DDOAB bilayer is initiated, the anisotropy is lowered significantly until complete solubilisation by Tween-20 takes place. Once the solubilisation is completed at Tween 20/DDOAB molar ratio of 2.15, no further structural change occurs and hence no change in the fluorescence anisotropy of the probe molecule is brought about. The values of saturation and solubilisation molar ratios obtained from fluorescence measurements were lower than those from DSC and turbidity experiments. This may be due to the combined hydrophobic effect of the bulky DPH and the nonionic Tween 20, that facilitates the early saturation and solubilisation of the DDOAB vesicles. The general series of events that follow upon mixing increasing amount of Tween 20 to the DDOAB vesicle is the same as that proposed by Lichtenberg for other lipid/surfactant systems. For example, the bilayer saturation followed by mixed micelle formation and finally complete solubilisation are the three stages involved in the complete vesicle to micelle transition.

In section 5.5 of the chapter, the effect of alkyltrimethylammonium bromides (*viz*; TTAB, CTAB and OTAB) on the thermal stability of DDOAB vesicle solutions have been investigated by DSC measurements on solutions containing fixed concentrations of DDOAB (5.0 mM) to which had been added varying concentrations of the additives. The results show that the gel-to-liquid crystalline phase transition temperature of aqueous DDOAB dispersion is dependent on the hydrocarbon chain length of the added surfactant. TTAB and CTAB, having chain length shorter than that of the lipid bilayer, decrease the  $T_m$  at all the

concentrations. On the other hand, OTAB having chain length similar to that of DDOAB, increased the thermal stability, thereby increasing the  $T_m$ . An important feature in the DSC thermogram of DDOAB / TTAB mixture was the presence of the peak at 36°C even upto a concentration of 1 mM. The retention of the pre-transition peak at 36°C was a clear indication that the gel-to-liquid crystalline phase transformation is not direct, but passes via the pre-transition. However, addition of CTAB and OTAB caused the disappearance of this peak showing evidence of direct transformation. Presence of TTAB and CTAB in excess of 1mM widened the main gel-to-liquid crystalline phase transition peak and in addition, new peaks appeared on the lower temperature side of the main peak showing evidence of more than one kind of domain within the vesicle. Some of the domains are rich in vesicle while some are rich in the added surfactant. Addition of OTAB even in very small concentration (0.5 mM) widened the peak. Though there were new peaks on the low temperature side of the main  $T_m$ , the main  $T_m$  is always more pronounced than the new peak. This indicates that the system is rich in DDOAB vesicles at all concentrations of OTAB.

The effect of some alkylpyridinium quaternary compounds on the  $T_m$  of DDOAB vesicles is also carried out and results were compared with the alkyltrimethylammonium counterpart having similar chain length. The surfactants chosen were hexadecylpyridinium halides ( $\text{Cl}^-$  and  $\text{Br}^-$ ; CPB and CPC) having equal tail length but with different head group geometry. The investigation highlights not only the effect of head group geometry, but also the counterion of the added surfactant on the gel-to-liquid crystalline phase transition temperature of the vesicle. The change in  $T_m$  induced by the addition of CPC and COB was small compared to CTAB in the measured concentration range, although the decreasing tendency of  $T_m$  is observable. This may be due to the greater ease of packing the planar pyridinium, compared to the tetrahedral trimethylammonium group into the vesicle. Moreover, CPC results in less perturbed vesicle structure and hence causes a smaller reduction in  $T_m$  compared to the addition of CPB. The ionic radii of  $\text{Cl}^-$  and  $\text{Br}^-$  are 0.181 nm and 0.196 nm respectively. Therefore, the charge on the more hydrated  $\text{Cl}^-$  is partially screened by the surrounding polar water molecules and these counterions are thus less effective in reducing the

charge repulsion among the head groups of the DDOAB vesicle. The  $\text{Cl}^-$  ions, therefore, cannot approach the highly charged surface of the vesicle as closely as less hydrated  $\text{Br}^-$  ions. Therefore, it can neither screen the charge at the surface of vesicles nor reduce the surface potential as effectively as  $\text{Br}^-$  (less hydrated ions). The overall effect resulted in less perturbed vesicle structure for the CPC/DDOAB system compared to CPB/DDOAB.

In the last section of the chapter, the influence of some selected hydroxyaromatic compounds viz; 1-naphthol, 2-naphthol, 2,3-dihydroxynaphthalene and 2,7-dihydroxynaphthalene on the  $T_m$  of DDOAB is examined. 1-naphthol, 2-naphthol, 2,3-dihydroxynaphthalene has a disordering effect on the thermal stability of the vesicle. This effect results in dramatic decrease in the  $T_m$ . Interestingly the reduction in  $T_m$  is more than that caused by the addition of surfactants. However, the effect of 2,7-dihydroxynaphthalene on the  $T_m$  of DDOAB is interesting. The  $T_m$  first decreased upto 2,7-dihydroxynaphthalene / DDOAB mole ratio of 1:1, and above this ratio there was an increase in the transition temperature. At higher molar ratios, the 2,7-dihydroxynaphthalene probably forms dimers within the hydrophobic region as a result of hydrogen bond formation between the OH groups of the additive. This result is supported by Density Functional Theory (DFT) calculations. The effective length of the molecule is thus increased and under this condition the length of the additive nearly matches the lengths of the vesicle forming surfactant chain and causes the  $T_m$  to increase.