Summary and conclusions

The aim of this Ph.D. thesis was to study the aqueous solution behavior of quaternary ammonium salt based conventional and gemini cationic surfactants. Special attention was focused on the effect of different organic additives viz. alcohols, diols, ethers with varying structures and hydrophobicity on micellar characterizations of surfactants. In addition mixed surfactant systems comprising of [i] nonionic (triton X-100)-cationic Gemini surfactants (12-s-12, s = 2,4 and 6) [ii] anionic (bile salts sodium cholate and sodium deoxycholate) – cationic (cetyltrimethylammonium tosylate) have been examined in detail.

Several techniques were employed in this work include physico-chemical (electrical conductance, surface tension, viscosity), spectral (NMR and SANS) and microscopic (Cryo-TEM) techniques to examine the self-assembly of cationic surfactants in the presence of different solvents and mixed systems with nonionic or anionic surfactants.

The thesis is divided into 9 chapters. While a general overview of surfactants and their solution, chemistry is provided in chapter1, chapter 2-9 concern with experimental studies carried out on cationic surfactants in aqueous media. Chapter 1 provides information on provides characteristic parameters of surfactant solution viz., Kraff temperature, cloud point, aggregation number, adsorption, micellization, critical micelle concentration etc. Effects of various factors such as temperature, salt, polar/nonpolar organic additive on micellization of surfactants are discussed. Mixed surfactant systems are also described in this chapter. Different physicochemical and instrumental techniques useful for characterization of surfactant solution behavior of are summarized.

Chapter 2 reports the investigation on the effect of spacer length on the micellization of six cationic gemini surfactant of the type 12-s-12 (s = 2, 4, 6, 8, 10, and 10). A systematic comparison between their micellar parameters, ( CMC, α, ΔGm, ΔHm, TΔSm, Nagg) adsorption parameters( area/molecule surfactant, efficiency and effectiveness) as a function of spacer carbon number is made using surface tension and conductance measurements, SANS was used to obtained information on micelle size/shape.

It was observed that CMC increase up to s = 4 and then it decreases; this trend was explain on the basis of conformational effect of the spacer. An increase in the α
value with an increase in spacer length indicates weak binding of counterion with the surfactant head as the s value increases. ΔG_m values manifest that the micellization is less favorable for s = 2 to 6 as compared to s > 6. ΔH_m values are negative for all gemini surfactants studied. An increase in ΔH_m is relatively more for s = 2 compared to s = 4 to 6 and can be understood by the change in hydrophobic interaction and hydration of surfactant molecule which depends on the spacer carbon number. The aggregation number for studied surfactants decreased with the increase in spacer length abruptly from s = 2 to 6, whereas for s = 6 to 10 it is almost constant and for s = 12 slightly increased again. The variation in the values of the A_min with spacer s is somewhat consistent with the variation in the CMC. The γ_CMC values increase up to s = 10; then for s = 12 it decreases slightly as compares to s = 10 due to the loop-like conformation of a spacer at the air-water interface.

In chapter 3 are presented results on aqueous solution of a cationic surfactant in the presence of two C_4 alcohols based on SANS, 2D NMR, conductance and viscosity experiments: It was concluded that the addition of the C_4 monohydric (1-butanol) and dihydric (1,4-butanediol) alcohols causes a change in the micellar properties of the surfactants in aqueous solutions. The CMC values indicate that both alcohols contribute to reduction in electrostatic as well as hydrophobic interactions, although these alcohols affect each surfactant in a differently. SANS results show variations in the manner in which these alcohols affect the micellization of the cationic gemini surfactant (12-4-12) versus the conventional cationic one (TTAB). Viscosity measurements indicate that micellar growth occurs as 1-butanol (C_4OH) is partitioned into both surfactant systems and has stronger tendency for micellar growth in the gemini surfactant system due to enhanced micellar properties and solubilization in the gemini amphiphile. The decrease in viscosity for 100 mM TTAB in the presence of [C_4OH] > 5% attributes to decrease in micelle size also supports SANS results for 100mM TTAB/10% C_4OH system. This observation leads to conclude that at higher C_4OH concentration, micelle–monomer equilibrium may shift towards monomers and hence the micellar size and N_agg decrease. Finally, the partitioning of the alcohols and their location in the micelles, as deduced from 2D NMR experiments, are consistent with the number and the position of hydroxyl groups on
the alcohol chain making a significant contribution to both hydrophobic and electrostatic aspects of the self-assembly process.

Study in chapter 4 revealed that the CMC of cationic surfactant in the presence of alkanediols (OH-(CH$_2$)$_n$-OH $n=2,4,6$ and 8) increased with progressive addition of diols except for 1,6-hexanediol (HD) and 1,8-octanediol (OD). 1,2-Ethanediol (ED) and 1,4-butanediol (BD) slightly enhance solubility of surfactant monomer hence both CMC and $\alpha$ increase. For HD and OD at lower concentration, the replacement of charged surfactant monomer leads to overall decrease in surface charge on micelle causing increase in $\alpha$ value and decrease in CMC thus favoring micellization. Changes in $^{13}$C chemical shift for surfactant in the presence different diols shows no appreciable interaction of ED and BD with surfactant and hence these diols influence by changing properties of solvent (water) while large chemical shift for HD and OD suggests adequate interaction with hydrocarbon tail of surfactant. SANS results in presence of all diols show a decrease in $N_{agg}$ and micelle size. For ED and BD, the transfer of surfactant tail is less spontaneous and results in lower $N_{agg}$. However, due to increased solubility of surfactant tail at higher concentration of HD and OD (10% and 5%, respectively), micelle-monomer equilibrium shifts towards monomer and results in reduction of $N_{agg}$. Thus, at lower concentration of these two diols, CMC of TTAB attributes that these diols interact with surfactant tail but as seen from SANS results at higher concentration they behave like short chain alcohol (dil) i.e. help in demicellization and reduce size and $N_{agg}$. Therefore, $C_6$ and $C_8$ diols function as cosurfactant or cosolvent depending on concentration. Further, comparison of micelle size and $N_{agg}$ in 10% HD and 5% OD suggests formation of relatively loose or less compact micelle in presence of OD.

Chapter 5 provides information on the effect of concentration of ethylene glycol and its oligomers as additives on micellization of a cationic surfactant in aqueous solutions and new data for $\Delta H_m$ and entropy $\Delta S_m$ for cationic surfactant in presence of diethylene glycol (DEG), triethylene glycol (TEG) and tetrathylene glycol (TeEG). For complete comparison data of ethylene glycol (EG) also provided. The CMC, $\alpha$, Gibbs energy of micellization ($\Delta G_m$) and Gibbs energy of transfer ($\Delta G_t$) of alkyl chain from bulk phase to micellar phase show linear increase with additive concentration. These observations lead to conclude that the presence of glycols
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reduces the micellization tendency of cationic surfactant. Comparison of thermodynamic parameters of micellization viz., $\Delta G_m$, $\Delta H_m$ and $\Delta S_m$ in the presence 10% of glycol oligomers suggests that thermodynamic tendency of micellization go in line with the presence of number of ethereal oxygen [-O-] in glycol oligomers, hydrogen bonding ability or water structure breaking ability of glycols and follows the order TeTG > TEG > DEG > EG. $\Delta G_m$ and $\Delta G_t$ are almost constant over the temperature range studied and Gibbs energy of micellization is more or less independent of temperature. $\Delta H_m$ becomes more negative and $\Delta S_m$ becomes less positive with increase in temperature resulting an enthalpy–entropy compensation for the micellization in all the studied systems.

Chapter 6 reports the CMCs of butanediyl-α,ω-bis(dimethyldodecyl-ammonium bromide) (12-4-12) in the presence of different alcohols measured by conductometry.

The presence of short chain alcohols viz. ethanol, 1,2-ethanediol and 1,4-butandiol enhance the solvent power of water for the gemini surfactant. The water structure breaking ability of these additive results in increasing CMC of 12-4-12. However, comparison of 1,4-butandiol with 1,2-ethanediol is quite contradictorily which is due to relatively good solvent power of 1,4-butandiol for hydrophobic chain of surfactant. On the other hand, long hydrophobic nonpolar chains for other alcohols allow their penetration in micelle such that -OH groups remain near palisade layer in contact with the bulk phase. Increased hydrophobicity of additives leads to decrease in CMC. The trends in results are well correlated with octanol–water partition coefficient ($P_{o/w}$) of alcohol additives. The CMC results in presence of isomeric butyl alcohols and hexanediol conclude that branching in alkyl chain (in C4OH) or shift of hydroxyl group (-OH) toward center of alkylene chain (in hexanediols) results in decrease hydrophobicity which in turn reflects decrease in CMC. 1,2-Ethanediol and 1,4-butandiol decrease the dielectric constant of water resulting in increase ionization of micelle i.e. degree of counterion dissociation ($\alpha$) increases. While for longer chain alcohols due to incorporation of chain in micelle, location of -OH group near palisade layer (micelle surface) and replacement of charged surfactant molecule by neutral alcohol molecule, leads to decrease overall surface charge on micelle.
causing increase in $\alpha$ values. NOESY study for 1% 1-butanol and 1% 1,4-butanediol confirmed that former interacts with micelle and penetrates toward micelle core (such that—OH group remain at micelle surface in contact with aqueous bulk phase) whereas 1,4-butanediol remain mostly in bulk phase.

Chapter 7 described the effects of ethylene glycol(EG), diethylene glycol(DEG) and their monoalkyl ethers (cellosolves and carbitols) and dimethyl ethers (glyme and diglyme) on micellization and micellar characteristics of a cationic surfactant (TTAB) in aqueous solution as observed from electrical conductivity and 2D NOESY show that these additives behave differently.

In water, the presence of glycols breaks up the ordered water structure by forming hydrogen bond with water molecules and decrease the dielectric constant of the solvent media. Thus, water-glycols mixtures behave better solvents than pure water and therefore the transfer of nonpolar tail of surfactant molecule from the bulk phase into the micelles is less favorable and increases CMC. Similarly, short alkyl chain ethers of EG and DEG (monomethyl, monoethyl and dimethyl) acts as codurfactants, remain mainly in aqueous bulk phase and increase CMC. The CMC decreasing effect seen for amphiliphilic monobutyl and monohexyl ethers is due to the formation of mixed micelles as these long alkyl chain ethers partition in micelles (behave as cosurfactant) and screen electrostatic interactions between charged head group of surfactant that favor decrease in CMC. However, the monobutyl ethers of EG and DEG may behave as cosolvent or cosurfactant depending on their concentration and solution conditions i.e. surfactant concentration, temperature, presence of salt. Usually at lower concentrations, these ethers behave as cosurfactant (decrease CMC) and at higher concentration more like cosolvent (increase CMC).

In chapter 8 studies on binary systems formed by the nonionic surfactant polyethylene glycol p-(1,1,3,3-tetramethylbutyl)phenyl ether (Triton X-100 or TX-100) and three gemini surfactants of the type alkanediyl-$\alpha$,$\omega$-bis (dimethyldodecylammoniumbromide) having similar tail length but varying spacer length have been reported. These are mostly based on surface tension data.

All three mixed systems showed strong synergism in their micellar properties viz. CMC, size, and aggregation number. According to Rubing’s regular solution theory, the interaction parameter, $\beta$ at all mole fractions for each mixed system was
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negative, thus indicating nonideality and synergism. The β becomes more negative with the mole fraction of TX-100 and increase in spacer length of gemini surfactant. Maeda’s approach suggests negative values of $\Delta G_m$ which indicate that mixed micellization is thermodynamically favored and mixed micelles are stable in the order TX-100 + 12-2-12 < TX-100 + 12-4-12 < TX-100 + 12-6-12. Mixed micelle size and the aggregation number from SANS also indicates the effect of the spacer length. The synergism and nonideality originate from the reduction in the electrostatic repulsion between the head groups of cationic gemini surfactants and the increase in steric repulsion of hydrophilic head groups of TX-100 as a function of the content of TX-100, and depend on the hydrophobicity of spacers and the polarity of the gemini surfactant head groups.

In chapter 9 Viscosity, cryogenic transmission electron microscopy (CryoTEM) and small angle neutron scattering (SANS) studies performed on mixed surfactant systems of bile salts viz., sodium cholate (NaC) sodium taurocholate (NaTC) and sodium deoxycholate (NaDC) and cetyltrimethylammonium tosylate (CTAT) showed strong interaction between these nonprecipitating anionic-cationic mixed systems. CTAT (critical micelle concentration $\approx 0.26$ mM and critical rod concentration $\approx 15$ mM at $30^\circ C$) shows remarkable increase in viscosity leading to visco-elastic stiff gel (at about 80 mM). The increase in temperature reverts viscosity increase favouring transformation to small micelles. The relative viscosity, $\eta_{rel}$, of CTAT solutions in water markedly decreases in the presence of small amount of trihydroxy bile salts (NaC, NaTC) reaching to a constant value close to that of water. However, for dihydroxy cholate, NaDC, a maximum in viscosity is seen after which it drops. The microstructure of CTAT micelles is altered by bile salts as revealed by cryoTEM. In aqueous solution the trihydroxy bile salt NaC transforms worm-like micelles of CTAT in to small mixed micelles without any growth or formation of vesicles or phase separation even at equimolar ratio as observed for oppositely charged mixed surfactants. The dihydroxy NaDC behaves differently, showing a maximum at intermediate concentration. In the presence of sodium chloride, CTAT-bile salt solutions showed an initial increase in viscosity but without precipitation in CTAT-NaDC even at equimolar solution. SANS results show the size and shape changes in mixed micelles. The results are discussed in terms of location of bile salt in
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mixed micelles. NaC with three –OH and a –COO groups remain in contact with bulk water that provide flat position for NaC molecules on micelle water interface. Such orientation increases the average area of the head group or the micelle curvature and reduces micelle size. On the other hand for NaDC, deoxycholate anion insert in cationic micelles, results decrease in micelle curvature (or average head group area) and consequently increase micelle size.