SUMMARY AND CONCLUSIONS

In the first part of the thesis, various physicochemical properties of single and mixed surfactants are reported. Such physicochemical characterization of micellar aggregates in aqueous solution could contribute to exploit in the field of fundamental as well as applied research. This involves the knowledge of a series of micellar parameters such as critical micelle concentration (CMC), micelle aggregation number (N_{agg}), degree of ionization of micelle (α), standard thermodynamic parameters of micellization such as ΔG°_{m}, ΔH°_{m} and ΔS°_{m}, interfacial parameters like the maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) including the standard thermodynamic parameters of adsorption. The performance properties of surfactants like foaming, wetting, cloud point, viscosity and detergency were also studied. All these properties are highly influenced by external factors such as temperature, pressure, pH, presence of additives etc.

The surfactant systems studied were nonionics Myrj 45 [polyoxyethylene (8) monostearate] and $C_{12}E_{10}$ [polyoxyethylene (10) lauryl ether], anionic surfactant sodium dodecyl benzene sulfonate (SDBS) and SDBS / $C_{12}E_{10}$ binary surfactant mixtures. Influence of temperature and different concentrations of additives on the above system was investigated. The additives were polyethylene glycol 400 (PEG 400), sucrose, urea and acetamide.

The critical micelle concentrations (CMC) for nonionic surfactants, Myrj 45 and $C_{12}E_{10}$ decreased as the temperature increases. This decrease in CMC with increasing temperature can be ascribed to various factors such as (i) the change in water structure around the ethylene oxide units; (ii) change in the hydrogen bonding networks around the ethylene oxide group; (iii) changes in the conformation of the oxyethylene moiety. However, for anionic SDBS the CMC was found to increase as temperature was increased. In general ionic surfactants have higher solubility at higher temperatures. Due to the disruption of water structure around the hydrocarbon portion of the surfactant molecule that opposes the micellization at higher temperatures higher is the CMC.

In presence of additives the micellization process was significantly altered. The formation of micelle is a result of hydrophobic interaction. It is also well known that the London dispersion is the main attractive force helping in the micelle formation. The additives break the three dimensional water matrix. Both PEG 400 and sucrose decrease the CMC of Myrj 45 and $C_{12}E_{10}$. These additives form structure with free water molecules as they have the hydrogen bond forming group i.e. they promote the water structure. The hydrophobic group of the surfactant too promotes the water structure leading to a decrease in the CMC of nonionics. It is to be noted that these additives although decrease the CMC, as the additive concentration increases the CMC too increases. The overall observed results can be attributed to various antagonistic factors like (i) formation of structure of water matrix due to hydrogen bonding ability of the additive; (ii) breaking of water structure by the presence of additives which leads to the formation of cavity in the liquid structure that can accommodate the molecules of additives; (iii) cosolubilization and mixed micelle formation; (iv) breaking of solvent structure with increase in temperature.

Urea is a well known water structure breaker and an efficient modifier of aqueous solution properties. For both Myrj 45 and $C_{12}E_{10}$ the CMC increases in presence of urea. As the water structure breaking property of urea is well known the effects of an increase in temperature and addition of urea should therefore be similar. The increase in CMC in presence of urea can be explained in terms of higher solubility of surfactant hydrophobic group, demicellization property and the stability of surfactant monomers in aqueous urea solutions. An interplay of all the above effects actually determine the overall result.

In case of sodium dodecyl benzene sulfonate (SDBS) the CMC increases in presence of polyethylene glycol 400 (PEG 400), sucrose and urea. In general the micelle structure may be considered to be made up of two regions, an outer region comprising of the polar head groups plus a portion of hydrocarbon chains in contact with water (i.e. the ionic heads fully and hydrocarbon chains to various degrees) and an inner region, the hydrocarbon core containing only all the remaining hydrocarbon chains not in contact with water. Both sucrose and PEG 400 due to their hydrogen bonding ability have major effect on water at the micellar - hydrocarbon water interfaces which is otherwise structured by hydrophobic effect. This leads to a poorer contribution to the hydrophobic interactions which is the driving force for the micellization, hence higher the CMC. The increase in the CMC of SDBS in presence of urea has been explained by the mechanism wherein urea replaces some water molecules that solvate the hydrophobic chain and the polar head group of the surfactant.

The CMC of SDBS / $C_{12}E_{10}$ mixtures at various mole fractions of 10:0, 9:1, 7:3, 5:5, 3:7, 1:9 and 0:10 at different temperatures of 35, 40, 45 and 50°C were determined. The effect of temperature on the CMC of the mixture was as observed for ionic surfactants i.e. CMC increased with increase in temperature. Therefore, one can surmise that mixed micelles are ionic in nature.

The critical micelle concentrations (CMC) of SDBS / $C_{12}E_{10}$ mixtures at 9:1, 5:5 and 1:9 mole fractions was determined in presence of different concentrations of PEG 400, sucrose and urea. The mixture CMC increased in presence of these additives. The overall effect of CMC has been attributed to various factors such as (i) breaking of water matrix by the additives; (ii) formation of structure in the solvent due to hydrogen bonding; (iii) electrostatic repulsions between the ionic species in presence of these additives.

The most important characteristic of surfactant solution is the micelle formation and a knowledge of energetics of the micellization process is very essential from both theoretical and practical point of view. The various thermodynamic parameters of micellization were evaluated using the phase separation model. The standard free energy change (ΔG°_m) of micellization was calculated using the relation

$$\Delta G^\circ_m = RT \ln CMC \text{ (for nonionics)}$$

$$\Delta G^\circ_m = (2-\alpha) RT \ln CMC \text{ (for ionics)}$$

CMC is in mole fraction scale and α, the degree of ionization of the micelle, ΔG°_m is the standard free energy change for the transfer of one mole of surfactant from solution to the micellar phase. The corresponding standard enthalpy (ΔH°_m) and entropy (ΔS°_m) of micellization per mole of the monomer were computed using the following relations -

$$\Delta H^\circ_m = -RT^2 \frac{d \ln CMC}{dT}$$

and

$$\Delta G^\circ_m = \Delta H^\circ_m - T\Delta S^\circ_m$$

The standard free energy of micellization (ΔG°_m) computed for all systems were negative both in presence and in absence of additives i.e. nonionic surfactants Myrj 45 and $C_{12}E_{10}$ and anionic sodium dodecyl benzene sulfonate (SDBS) and SDBS / $C_{12}E_{10}$ mixed surfactant system. Such negative ΔG°_m values indicate spontaneous micelle formation. For SDBS and $C_{12}E_{10}$ mixed system at all the mole fractions studied the ΔG°_m showed larger negative values than either of the pure components. This indicates that the mixed micelle formation is favoured. Moreover a minimum observed at $N_{SDBS} = 0.1$ implies mixed micelle stability. However, in presence of various concentrations of PEG 400, sucrose and urea ΔG°_m values are less negative than in their absence for SDBS / $C_{12}E_{10}$ mixed system, suggesting that mixed micelle formation is relatively more favoured in absence of additives. The ΔG°_{m} becomes more and more negative as the temperature increases indicating that mixed micelle formation is more spontaneous at higher temperatures. In case of additives present in the system the changes observed in ΔG°_{m}, may be ascribed to their pronounced effect on water structure.

The standard enthalpy of micellization (ΔH°_{m}) values indicate that the overall micellization process is exothermic although an endothermic contribution is observed in case of pure nonionic surfactants Myrj 45 and $C_{12}E_{10}$. The exothermic and endothermic characteristics of micellization are specific to surfactant, additive and temperature. The overall independence in ΔH°_{m} can be attributed to the fact that there does not occur a remarkable change in the environment surrounding the hydrocarbon chain of the surfactant molecule in presence of additive as the temperature is changed. The ΔH°_{m} quantity was mostly independent of temperature and increasing additive concentration. This may also be due to the error associated with ΔH°_{m} (i.e. ± 10%).

The entropy of micellization (ΔS°_{m}) was positive in all cases, and the value was very high for pure nonionic surfactant Myrj 45 and $C_{12}E_{10}$. Such positive contribution to the entropy changes indicate that the micellization process is somewhat entropy dominated. Also, higher entropy changes are generally accompanied by a phase change and micelles are assumed to be in separate phase. The higher entropy changes, ΔS°_{m} are ascribed to greater randomness in the hydrocarbon chains in the micelle interior. However, it is not very clear how this movement of the hydrocarbon chains in the core of the micellar aggregates can have a dominating effect on ΔS°_{m}, which is a macroscopic property. The higher ΔS°_{m} values even in presence of additives indicate that the additives still control the three dimensional water matrix.

A linear correlation was observed between enthalpy and entropy of micellization for all the solvent systems. The ΔH°_{m} - ΔS°_{m} plot yielded a slope of ~ 320 K suggesting

that at this temperature i.e. isostructural temperature, the micellization process is fully independent of any structural factors and depends entirely on enthalpic forces.

The transfer enthalpy of micellization ($\Delta\Delta H^{\circ}{}_{m}{}^{tr}$) which is sensitive to the solvent structure was also computed using the following relation -

$$\Delta\Delta H^{\circ}{}_{m}{}^{tr} = \Delta H^{\circ}{}_{m}\ (\text{aq. additive}) - \Delta H^{\circ}{}_{m}\ (\text{water})$$

For all systems studied, the $\Delta\Delta H^{\circ}{}_{m}{}^{tr}$ values were negative which can be attributed to surfactant hydrophilic group additive interactions.

From the surface tension data the adsorption parameters like maximum adsorption density (Γ_{max}) and minimum area per molecule (A_{min}) were evaluated. The Γ_{max} values were found to increase as temperature increases due to the dehydration of oxyethylene chains. But in case of ionic surfactant, Γ_{max} decreased with rise in temperature. For SDBS / $C_{12}E_{10}$ mixed system., the Γ_{max} values at all mole fraction were found to be in between that of the pure components.

The minimum area per molecule (A_{min}) decreased for nonionics and increased for ionics with rise in temperature. The higher values observed in ionics is due to mutual repulsion between the surfactant molecules due to thermal agitation. However, lower A_{min} values were observed for these surfactant systems in presence of additives. This may probably be due to reduced repulsions between the oriented ionic head groups allowing a closer packing at the air / water interface. The overall effect has been ascribed to factors such as (i) changed structure of the head group due to surfactant - additive interaction; (ii) changed nature of the solvent due to the presence of additives; (iii) the presence of additives at the air / water interface.

The standard thermodynamic parameters of adsorption for all the systems were evaluated. The ΔG°_{ad} values were all found to be negative implying spontaneous process of adsorption. However, it is to be noted that ΔG°_{ad} values were always more negative than the corresponding ΔG°_m values which indicates that adsorption process is relatively more favoured than micellization. Moreover, ΔG°_{ad} was always found to be more negative with rise in temperature in presence as well as in absence of additives. Dehydration of the hydrophilic group is required for the adsorption to take place, since at higher temperatures the surfactant is less hydrated, comparatively, lesser energy is required for adsorption. The standard enthalpy of adsorption (ΔH°_{ad}) indicates both exothermic and endothermic contributions. Such exothermic/endothermic contributions towards adsorption process can be ascribed to whether bond making or bond breaking predominates during adsorption. The entropy of adsorption (ΔS°_{ad}) was overall positive for all systems indicating a greater randomness in the hydrocarbon chains at the interface.

The cloud point is a characteristic of nonionic surfactants. It has been found that both PEG 400 and sucrose decrease the cloud point of Myrj 45 and $C_{12}E_{10}$ and increase in presence of urea. This is because the additives compete for the water molecules with the micelles and the surfactant becomes less and less hydrated and thereby lowers the cloud point. Urea, however increases the cloud point by making itself to interact with the polyoxyethylene chains of the nonionic surfactant. In presence of sodium dodecyl benzene sulfonate (SDBS), an anionic surfactant, the cloud point increases. This is due to the formation of mixed micelles that are charged in nature, the repulsive forces are more prominent and therefore higher is the temperature required for clouding.

The micellar aggregation number (N_{agg}) was determined by steady state fluorescence quenching method. The N_{agg} were found to be higher for the SDBS / $C_{12}E_{10}$ mixtures than pure SDBS and $C_{12}E_{10}$. In presence of PEG 400, sucrose and urea, the N_{agg} value decreased at all the additive concentrations. The overall effect is indicative of the hindrance in the micelle formation due to the presence of these additives at the micelle solvent interface.

The interaction between the surfactant molecules in the mixed micelles were evaluated by Rubinghs approach. The β^m values thus obtained for SDBS / $C_{12}E_{10}$ system was negative throughout implying an attractive interaction. This may be due to the interaction between the oxonium ion of nonionic polyoxyethylene and the anionic surfactant. In presence of additives the β^m are less negative which indicates that the attractive forces between the surfactant molecules decrease due to the presence of additives. Moreover, β^m values becomes less and less negative as temperature increases due to greater repulsion between the ionic heads in the mixed micelles.

The partition coefficient of neutral additives between the micelles and water were computed from the variation of critical micelle concentration (CMC) of the surfactant on the addition of additives. The micellization constant, K_M values calculated for all the systems were negative and hence the ideal partition coefficient was almost zero in case of all these surfactant - additive system. The additives PEG 400, sucrose, acetamide and urea are all non-penetrating ones and they can be assumed to have located themselves at the micelle-solvent interface.

The proton nuclear magnetic resonance (^{1}HNMR) was also used to study the mixed surfactant behaviour. It shows an evidence of an interaction between the oxyethylene moiety of $C_{12}E_{10}$ with the benzene ring of SDBS. The proton spin lattice relaxation time (T_1) determined at different SDBS mole fractions indicates a restricted motion of oxyethylene chains at lower SDBS mole fraction and the micellar structure loosens up at higher N_{SDBS} due to mutual coloumbic repulsions between the ionic heads in the mixed micelle.

The various performance properties of the surfactant systems like foaming, wetting, viscosity and detergency were also investigated and discussed in the second part of the thesis. The intrinsic viscosity [η] decreased as temperature increases for pure $C_{12}E_{10}$ due to the dehydration of polyoxyethylene moiety. However, in presence of PEG 400 and urea a higher [η] value was obtained compared to that in presence of sucrose. The volume of the hydrated micelle, V_h and that of the oxyethylene unit (V_{OE}) increased in presence of PEG 400 and urea and decreased in presence of sucrose.

The [η] value of 2.5-4 cm^3/g indicates a globular particle. In presence as well as in absence of additives for SDBS and $C_{12}E_{10}$, the [η] value is above 5 cm^3/g implying a non-spherical particle. For SDBS / $C_{12}E_{10}$ mixed system a positive deviation from linearity is observed in relative viscosity - SDBS mole fraction plot. This suggests a mixed micelle formation. In presence of additives too this deviation from ideality is present although the intrinsic viscosity [η] show changes at lower SDBS mole fraction in the surfactant mixture. The thermodynamic activation parameters for the viscous flow was computed from Frenkel-Eyring equation. Almost a constancy in $\Delta G_{VIS}^{\neq}$ at various additive concentrations indicate that additives do not show any effect in the viscous flow with increasing concentrations.

Foaming is an inherent property of surfactants solution. The foaming efficiency of sodium dodecyl benzene sulfonate (SDBS) was higher than nonionic surfactants, Myrj 45 and $C_{12}E_{10}$. The initial foam height in case of Myrj 45 was too low to be measured. In presence of additives little variation in the initial foam height for $C_{12}E_{10}$ was observed. The SDBS / $C_{12}E_{10}$ surfactant showed a somewhat synergistic behaviour in foaming. The foaming efficiency of nonionic $C_{12}E_{10}$ was enhanced in presence of anionic SDBS. Increase in temperature decreased the foam height for nonionics and increased for ionic surfactants.

Detergency is one of the most important property of surfactant systems. The detergency studies were carried out by dye solubilization technique. The nonionics Myrj 45 and $C_{12}E_{10}$ showed maximum dye removal efficiency as expected for nonionic surfactants due to their low critical micelle concentration (CMC) and also are better solubilizing agents than ionics in dilute solution. The additives PEG 400, sucrose and urea lowered the dye removal efficiency of both ionic SDBS as well as nonionic surfactants studied. However, in case of SDBS / $C_{12}E_{10}$ mixture the dye removal efficiency of ionic SDBS increased in presence of nonionic $C_{12}E_{10}$ probably due to the interaction of the polyoxyethylene chains with the benzene sulfonate group, an overall synergistic effect.

The contact angle 'θ' determined for the surfactant systems reduced in presence of PEG 400, sucrose and urea indicating a lowering of interfacial energy of the solid / liquid interface, suggesting an interaction of the additive with the surfactant. The wetting efficiency of the mixed SDBS / $C_{12}E_{10}$ system was actually lower than that of the pure components. Hence, one can postulate that the wetting characteristics of the surfactant solution depends on the amount of each component and the presence of additives since it is the surface activity change which regulates the contact angle.