Chapter VII

Summary

The intrinsic duality of Surface Active Agents (Surfactants) due to the presence of both hydrophilic and hydrophobic moieties is responsible for spontaneous self aggregation of surfactant molecules into finite sized molecular entities such as micelles as well as for their use in solubilization, catalysis, dispersion, biochemical and pharmaceutical formulations. Surfactants are also important for chemical and biochemical research as well as for controlled drug release, stability of pharmaceutical dosage forms, nanomaterial synthesis, firefighting, preconcentration of analytes prior to chromatography etc. However, surfactant systems used for practical applications mostly consist of mixtures of surfactants, either because commercial surfactants are always mixtures due to the raw materials used and method of manufacture or because mixtures of surfactants often show better performance properties than individual surfactants. Addition of nonionic surfactant to an ionic surfactant solution may significantly lower the cmc and may also increase the size of the micelle and ultimately affects the micellization behaviour and also help in optimizing the properties as compared to that of a single surfactant. Hence, in complex world of surfactant formulation, surfactant technologists need to have working knowledge to predict and manipulate –

i)   tendency of surfactant to self aggregate into micelle as reflected from cmc.

ii)   The shape and size of the micelle, which directly controls the rheological properties of micellar solutions that are important in personal care products.

Thus, a clear understanding of the underlying physics and chemistry of mixed surfactant systems is inevitable and highly desirable from fundamental as well as industrial point of view, so as to optimize and tune the micellar properties for a desired application. With all these points in sight, we studied various different combination of surfactant mixtures, and our observations are presented in the first half of the thesis (i.e., chapters II – V).

Fatty acid methyl ester based surfactants, which have peculiar characteristics like i) quick availability from renewable vegetable material ii) good biodegradability iii) superior detergency for fabrics iv) good tolerance against calcium ions were mixed with nonionic surfactants of polyoxyethylene alkyl ether type abbreviated as C_nE_m, which are widely

used as i) detergents ii) solubilizers and iii) emulsifiers, in order to optimize the biodegradability and minimize toxicity and formulating a detergent which is effective in hard water.

A detailed investigation of various physicochemical properties of the following anionic-nonionic surfactant mixtures –

1) Hexaoxyethylene monododecyl ether ($C_{12}E_6$) - α-sulfonato myristic acid methyl ester (MES).

2) Hexaoxyethylene monododecyl ether ($C_{12}E_6$) - α-sulfonato palmitic acid methyl ester (PES).

3) Nonaoxyethylene monododecyl Ether ($C_{12}E_9$) - α-sulfonato myristic acid methyl ester (MES).

4) Nonaoxyethylene monododecyl ether ($C_{12}E_9$) - α-sulfonato palmitic acid methyl ester (PES)

was carried out. All these combinations also helped us to verify the effect of change in hydrophilicity (or ethylene oxide content, i.e., $C_{12}E_6$ and $C_{12}E_9$) as well as variation in hydrophobicity (i.e MES and PES) on the micellization process as well as its impact on the physicochemical and performance properties.

Chapters II-V, deal with the detailed investigation of following physicochemical properties of different surfactant mixtures. The physicochemical characterization involved determination of,

A) critical micelle concentration of single as well as mixed surfactants of different mole ratios by surface tension as well as conductivity measurements,

B) degree of ionization of micelle (α) of ionic surfactant,

C) thermodynamic parameters of micellization ($\Delta G_m^0, \Delta H_m^0$ and ΔS_m^0) as well as adsorption (ΔG_{ad}^0, ΔH_{ad}^0 and ΔS_{ad}^0) of surfactants at the air/water interface,

D) maximum surface excess ($\Gamma_{max.}$) and minimum surface area per molecule of surfactant ($A_{min.}$) at the air/water interface,

E) micellar aggregation number($N_{agg.}$)by steady fluorescence quenching method,

F) micropolarity indicative of solubilization and polarity around fluorecent probe in mixed micelles,

G) interaction between surfactant molecules in the mixed micelle and composition of mixed micelle by Rubingh's treatment,

H) performance properties like viscosity, foaming and detergency.

Moreover, the interaction between the surfactant molecules in the mixed micelle was also studied using ^{1}H NMR measurements, and recent treatment proposed by Maeda, which emphasizes on the chain-chain interaction of surfactants for $C_{12}E_6$/PES mixed surfactant system.

The critical micelle concentration (cmc) value for nonionic surfactants, $C_{12}E_6$ and $C_{12}E_9$ decreased with increasing temperature. This decrease in cmc with increasing temperature is ascribed to various factors such as i) the change in water structure around the ethylene oxide group ii) change in the hydrogen bonding networks around the ethylene oxide groups iii) changes in the conformation of the ethylene oxide group iv) dehydration of hydrophilic groups. However, for ionic surfactants i.e., MES and PES, the cmc increased with increasing temperature. This may be due to disruption of strucured water around the hydrophobic group and increased solubility of surfactant, which opposes micellization. The cmc values of binary combinations of $C_{12}E_6$/MES, $C_{12}E_6$/PES, $C_{12}E_9$/MES and $C_{12}E_9$/PES fall beween the individual cmc values of the constituent surfactants. However, the cmc values at $N_{PES} = 0.1$ for $C_{12}E_6$/PES and $C_{12}E_9$/PES surfactant mixtures are lower than the cmc values of the individual surfactants, indicating synergistic interactions between the constituent surfactants of the binary combinations.

The most important characteristic of surfactant solution is micelle formation and a knowledge of energetics of micellization process is very essential from both theoretical and

practical view points. The various thermodynamic parameters of micellization ($\Delta G_m^0, \Delta H_m^0$ and ΔS_m^0) were evaluated using the phase seperation model. The standard free energy of micellization (ΔG_m^0) computed for all the mixed systems were negative and became increasingly negative with increasing temperature. Such negative ΔG_m^0 values indicate spontaneous micelle formation and spontaneity increases with increasing temperature. The standard enthalpy of micellization (ΔH_m^0) values indicate that the overall micellization process for $C_{12}E_6$/MES, $C_{12}E_9$/MES and $C_{12}E_9$/PES systems is endothermic, although a exothermic contribution is observed for MES and PES. However, the micellization process was exothermic for most of the mole ratios of the two surfactants for $C_{12}E_6$/PES surfactant mixture. For almost all nonionic surfactants, cmc decreases as the temperature increases, i.e., thermodynamically the system is endothermic. In case of $C_{12}E_6$/PES surfactant mixture, as more and more PES was added, the micellization process changed from endothermic to exothermic. The surfactant molecule-water and water-water interactions both change continuously as the composition of the mixed micelle changes. The ΔH_m^0 values declined as the mole fraction of PES in the mixed system increased. This implies a change in the environment surrounding the hydrocarbon chain of the surfactant molecules. The entropy of micellization (ΔS_m^0) was positive in all cases, and the value was very high for pure $C_{12}E_6$ and $C_{12}E_9$. Such positive contribution to the entropy changes indicates that micellization process is somewhat entropy dominated. Also, higher changes in ΔS_m^0 are generally accompanied by a phase change and micelles are assumed to be a separate phase. The higher entropy changes are ascribed to greater randomness in the hydrocarbon chains in the micelle interior. A linear correlation between enthalpy (ΔH_m^0) and entropy of micellization (ΔS_m^0) was observed for all the mixed surfactant systems and the compensation temperature was derived from the slope of the ΔH_m^0-ΔS_m^0 plots as suggested by Lumry and Rajender. At compensation temperature or the isostructural temperature, the micellization process is independent of any structural factors and depends entirely on enthalpic forces. The magnitudes of the compensation temperature for various different

mixed surfactant systems are observed to be within the temperature range suggested in literature. Similar enthalpy-entropy compensation phenomenon was also observed for process of adsorption of surfactants at the air/water interface.

The surface excess concentration under the conditions of surface saturation ($\Gamma_{max.}$) is a measure of maximum extent of adsorption of surfactants at the air/water interface. The Γ_{max} increases with increasing temperature for nonionics whereas, it decreases for ionic surfactants. The increase in Γ_{max} for nonionic surfactant is due to decreasing hydration of ethoxy segments leading to greater tendency to locate at the air/water interface. The decrease in Γ_{max} with increase in temperature for ionics may be due to higher solubility of ionic surfactants, which opposes adsorption of surfactants at the air/water interface. The minimum area per molecule of surfactant at the air/water interface (A_{min}) decreases for nonionics and increased for ionics with rising temperature. The higher values observed in case of ionic surfactants are due to mutual repulsion between the surfactant molecules due to thermal agitation. Whereas, for all the mixed systems lower values of $A_{min.}$ (< 1 nm^2) were obtained. The lower A_{mm} values are attributed to closer packing at the air/water interface owing to decreased repulsion between the oriented headgroups in binary combinations.

The standard thermodynamic parameters of adsorption of surfactants at the air/water interface were evaluated. All the ΔG_{ad}^0 values were negative, implying spontaneous adsorption process. However, it is also noteworthy that ΔG_{ad}^0 were always more negative than the corresponding ΔG_m^0 values suggesting that micellization occurs only after the interface becomes saturated with the monomeric surfactant. The standard enthalpy (ΔH_{ad}^0) indicates exothermic and endothermic contributions. Such exothermic/endothermic contributions towards adsorption process can be ascribed to either predominance of bond making or bond breaking during adsorption. All the values of entropy of adsorption of surfactants at the air/water interface (ΔS_{ad}^0) are positive reflecting greater freedom of motion of hydrocarbon chains of surfactant monomers at the planar

air/water interface compared to that in the cramped interior beneath the convex surface of the micelle.

The micellar aggregation number ($N_{agg.}$) values were determined at different mole ratios of the binary surfactant mixtures. The micellar aggregation number of mixed surfactant systems were intermediate to that of individual surfactants, though a regularity was difficult to visualize. The ratio of the first and the third vibronic peaks i.e, I_1/I_3 in a monomeric pyrene fluorescence emission spectrum is sensitive to local polarity around the fluorescent probe. The intensity against wavelength (emission) plots yielded I_1/I_3 values. The I_1/I_3 values for all the mixed systems, suggesting polar surroundings around pyrene in the micelle interior.

Rubingh's non-ideal solution theory was used to evaluate β^m - a measure of interaction between the constituent surfactant molecules in the mixed micelle. The β^m values were found to be negative for all the systems, suggesting attractive interactions between the anionic and nonionic surfactant molecules in the mixed micelle. This interaction is due to attraction between the weak cation of nonionic surfactant of poly (ethylene oxide) class [resulting either from oxonium ion formation with protons from water or sharing of the hydrogen in water by hydrogen bond formation] and the anionic surfactant. The composition of the mixed micelle was also estimated. The sum of the activity coefficient of ionic and nonionic surfactant in the mixed micelle was never unity suggesting deviation from ideal behaviour. β^m determined by regular solution approach of Rubingh explains the long range electrical interaction between the surfactant headgroups in the mixed micelle. However, recently Maeda suggested that there are chain-chain interactions present in a mixed system in addition to head group head group interactions. He proposed another interaction parameter B_1 that encompasses the hydrocarbon chain-chain interactions and is also responsible for the stability of the mixed micelle. For $C_{12}E_6$/PES mixed surfactant system, the attractive interaction between $C_{12}E_6$ and PES in the mixed micelle was explained using ^1H nuclear magnetic resonance measurements as well as Maeda's concept. The B_1 values for $C_{12}E_6$/PES system are negative indicating that chain-chain interaction contributes to the stability of the mixed micelle. In this case, ionic

surfactant has a hydrophobic chain of 14 carbons whereas, the nonionic surfactant has 12 carbon atoms and thus contributes to chain-chain interaction. However, the headgroups are hydrated and if the water molecules of one hydration shell are also the part of another hydration shell i.e., the water molecules act as a bridge between the surfactant molecules just below the water-micelle interface, then also the attractive interactions will ensue. The free energy of micellization evaluated using Maeda's concept and that of phase seperation model are in good agreement with other suggesting that the counterion bindings are very high in the $C_{12}E_6$/PES mixed system and hence no break point is observed in the conductance-concentration profile.

The performance properties viz. viscosity, foaming and detergency were also studied. The detergency studies did not reveal any synergistic behaviour in this phenomenon for $C_{12}E_6$/MES mixed system. Foaming and viscosity were found to depend on solution compostion dependent. Although temperature had an impact on foaming efficiency, it had negligible effect on the viscosity of the mixed surfactant systems. The foaming efficiency for mixed systems was found to be superior than that of nonionic surfactants. The intrinsic viscosity values suggested that at all the mole fractions of the binary surfactant combinations, the mixed micelles were non-spherical or elongated. The viscosity of nonionic surfactant solution of $C_{12}E_6$ increased tremendously on addition of NaCl.

Cloud points (CP) are manifestations of solvation/desolvation phenomena nonionic surfactant solutions. At cloud point, the nonionic surfactant is no longer soluble in water and solution becomes hazy or cloudy. This instant seperation of nonionic surfactant upon heating into two phases, one surfactant rich and other aqueous, containing surfactant close to cmc at that temperature is a characteristic of nonionic surfactant, which differentiates it from ionic surfactant. CP is very sensitive to presence of additives in a system, even at very low concentrations.

The cloud point (CP) determination of for $C_{12}E_6$ (1% w/v) solution was carried out in presence of poly ethylene glycols of different molecular weight (MW 200, 300 and 400) as well as in presence of increasing amounts of ionic surfactant PES. The PEGs had negligible effect on CP of $C_{12}E_6$. However, the CP increased in presence of PES, even

though the concentration of PES was very low. Such behaviour may be due to the formation of charged mixed micelles. This would result in repulsion between the micelles hindering their aggregation thereby raising the CP. The effect of various tertraalkylammonium bromides having different alkyl chains on the CP of 1% w/v $C_{12}E_9$ solution was also studied. It was observed that tetramethylammonium bromide (TMAB) decreases the CP of $C_{12}E_9$, tetraethylammonium bromide (TEAB)does not affect the CP much, whereas tetrapropylammonium bromide (TPAB) and tetrabutyammonium bromide (TBAB) increase the cloud point. The decrease in CP of $C_{12}E_9$ in presence of TMAB is due to its water structure forming property. Whereas, CP increase due to TPAB and TBAB is ascribed to dominance of mixed micelle formation these ions with nonionic surfactant over its water structure forming capability.

Chapter VI A of the present thesis deals with the study of the effect of additives on the cloud point of nonionic surfactants $C_{12}E_6$ and $C_{12}E_9$. The effects of various electrolytes and nonelectrolytes on the cloud point of $C_{12}E_6$ and $C_{12}E_9$ were studied. It was observed that NaCl, NaI, KCl, KBr, and tetraethylammonium iodide do change the cloud point to a large extent. Water structure breaking property of NaI and KI is responsible for its effect different from that of NaCl, NaBr as well as KCl and KBr. The CP of $C_{12}E_9$/TX 100 (2% w/v) nonionic surfactant mixture was also determined and the mixed surfactants showed clouding phenomena at temperatures, which were intermediate to that of corresponding individual surfactants.

Chapter VI B of the thesis deals with the development of a membrane selective electrode sensitive towards a cationic surfactant in aquo-organic medium. The electrode which was originally sensitive towards dodecyltrimethylammonium ions (DTA^+) was proved to be sensitive to tetradecyltrimethylammonium ions (TTA^+) and was also used for determination of critical micelle concentration of tetradecyltrimethylammonium bromide in water as well as aquo-organic media (i.e., water/dimethyl formamide and water/dimethyl sulfoxide mixture, upto 40% v/v of the organic liquid). The response of the electrode was observed to be Nernstian in the aquo-organic medium and its validity for electrochemical measurements was substantiated by comparable values of cmc of TTAB obtained using

this electrode, with those obtained by conductivity measurements in aquo-organic media. The cationic surfactant ion selective electrode showed good resistance towards the mixed solvent system (within the concentration range studied) and can prove to be an important additional tool for studying the self aggregation of cationic surfactants in aquo-organic medium.