PHYSICOCHEMICAL PROPERTIES OF NONIONIC SURFACTANTS IN PRESENCE OF ADDITIVES

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The unique chemical structure of surfactant molecules 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 numerous uses in the fields of industrial and commercial application like in solubilization, catalysis, dispersion, biochemical and pharmaceutical formulations. The physicochemical, performance and microstructural properties of surfactants are very sensitive and are influenced or tuned to a desired range, shape and application by altering the solution condition such as concentration, temperature, pressure, *p*H and the presence of another surfactant or foreign substances (additive/co-solvent/co-surfactant). Such aggregates are formed in various shapes e.g. globular, ellipsoidal, cylindrical and disc like. Mixtures of surfactants form mixed micellar aggregates, which are superior to that of those of the individual components. It is thus of interest to examine the micellar solution properties of nonionic surfactants in presence of various additives and with the new types of surfactant i.e. gemini surfactant.

The Polyoxyethylene alkyl ether type surfactants abbreviated as C_nE_m are most widely used nonionic surfactants in detergency, cosmetics, solubilization, deinking, emulsion formation like shampoo and conditioners as well as in pharmaceutical dosages and in drug delivery and will continue in the future due to their higher solubility at low temperature. Gemini surfactants are recently developed and not much work has been done in their micellar behaviors. They consist of two hydrophobic chains and two hydrophilic groups covalently attached through a spacer, which make them attracting considerable interest in both academic and industrial research in the recent years. There superior properties suggest that they are possible candidate for the next generation of the surfactants. Gemini surfactants are currently under extensive investigation for their possible use in formulation mixing with ionic, nonionic, zwitterionic and other surfactants.

The thesis described the physicochemical, performance and micro structural properties of nonionic surfactants in the presence of various additives and investigation of physicochemical properties of binary surfactant mixture of gemini and nonionic surfactants. The contents of the thesis are divided in to eight chapters. Chapter I gives an introduction and literatures review to the surfactant and micellar solutions. Chapters II and III, deal with the detailed investigation of physicochemical properties of binary surfactant mixture of gemini and nonionic surfactants *viz.* 1,4-butanediyl-α,ω–bishexadecyldimethylammoniumbromide, 16-4-16, $2Br^-$ and 1,10-decanediyl α–ω bishexa decyldimethylammoniumbromide, 16-10-16, $2Br^-$ with POE nonionic surfactants having similar hydrophilic moiety and different hydrophobic tail $C_{12}E_6$, and Triton X-100. We also investigated the self aggregation of cationic-nonionic, TTAB and Brij-35 binary surfactant systems, which is present in Chapter III. Chapters IV – VII present the physicochemical, performance and microstructural properties of nonionic surfactants in the presence of various additives, *viz.* $C_{12}E_9$: amino acids (glycine, alanine, valine), $C_{12}E_{10}$: sugars (ribose, glucose, sucrose), $C_{12}E_{10}$: alcohols (EtOH, PrOH, BuOH, PenOH) and $C_{12}E_{10}$: *p*H . In the end, a summary is given in Chapter VIII (this chapter).

Chapter I gives an introduction to the surfactant and micellar solution. The thermodynamics of the formation of micelles, structures (shape and size), and methods to investigate the micellar solution are discussed. We have also discussed the ideal and nonideal theory of mixed surfactant systems. The various methods for studying the structures of micellar solution are also discussed. In this connection a brief discussion on small-angle neutron scattering and dynamic light scattering is given.

Chapters II and **III**, deal with the detailed investigation of following physicochemical properties of mixed surfactant systems.

1) Krafft temperature by solubility measurement.
2) Critical micelle concentration (CMC) of single as well as mixed surfactants of different mole ratios by surface tension measurement. For TTAB: Brij35 surfactant system the CMC of different binary mixtures were investigated by

surface tension and also by conductance measurements.

3) Micellar Aggregation number (N_{agg}) by steady state fluorescence quenching technique.
4) Micropolarity - indicative of solubilization and polarity around pyrene in mixed micelles.
5) Interaction parameters at the monolayer state at the air – water interface (β^{σ}) as well as at the mixed micelle (β^{m}) –by Rubingh's treatment.
6) Dynamic Light Scattering (DLS) measurements.

In addition to the investigations mentioned above, we also studied the interaction between the surfactant molecules in mixed micelle by the recent theory of Maeda, which emphasizes on the chain-chain interaction of surfactants.

Chapters IV-VII, deals with the detailed investigation of the following,

1) Phase diagrams of $C_{12}E_9$ and $C_{12}E_{10}$ by cloud point measurements.
2) CMC of surfactant in the presence and absence of above mentioned additives at different concentrations by surface tension measurements at different temperatures.
3) Thermodynamic parameters of micellization (ΔG_m^0, ΔH_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 in presence and absence of additives.
4) We also computed and discussed the Heat capacity ($\Delta C_{p.m}$), Transfer enthalpy ($\Delta H_{m.tr}$), and Transfer heat capacity ($\Delta C_{p.m.tr}$), of micellization in presence and absence of additives.
5) Maximum surface excess ($\Gamma_{max.}$) and minimum surface area per molecule (A_{min}) of surfactant at the air/water interface are also determined.
6) Structural investigation like shape, size, number density of micelle and aggregation number (N_{agg}) of $C_{12}E_9$ micelle in absence and the presence of different amino acids (glycine, alanine, valine) and $C_{12}E_{10}$ micelle : sugars (ribose, glucose and sucrose) at different temperatures by Small Angle Neutron

Scattering (SANS) measurements.

7) The shape of micelle was also determined by viscosity measurements.

8) DLS measurements were carried on $C_{12}E_9$: Amino Acid systems.

In **Chapter IV b**, we have investigated in detail the effect of various electrolytes, nonelectrolytes and TX 100 on the phase separation of $C_{12}E_{10}$ micellar solution.

The interaction between the additives and surfactant molecules was also studied using ^{1}H-NMR measurements.

It was observed that the cmcs of nonionic surfactants as well as of gemini surfactants, decrease with increasing temperature. The cmc values of mixed surfactant systems at any mole ratio were found lower than either of pure surfactants, indicating a synergistic behavior. The 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. The cmc values of binary combinations of TTAB/Brij 35 fall between the cmc values of the constituent surfactants, though the cmc variation with mole fraction of TTAB is not linear. For 1:1, TTAB/Brij 35 system, surface tension and fluorescence method gave same cmc values, but cmc value obtained by conductance is much higher. However, γ - $\log_{10}C$ plot does show a dip around the same value, where conductance shows a break. This may be due to the second state of aggregation, which arises because of change of shape of a micelle, which has also been observed by QELS measurements. We have reported the evidence for existence of second state of aggregation of 1:1 and 8:2, TTAB/Brij 35 mixed surfactant system. The first cmc corresponds to the normal spherical micellar aggregates formed by the association of surfactant monomers at a critical concentration. Whereas, the second state of aggregation represented by the second CMC is due to structural transformations at surfactant concentrations well above the CMC. The structure breaking ability of amino acids and its interaction with the oxyethylene groups of the surfactant were dominating factor in the micellization process in the case of aquo-amino acids $C_{12}E_9$ systems. It is observed that at constant temperature, cmc has increased with *p*H of the solution; low *p*H favoured the micellization of the surfactant. It is also found that the CMC of $C_{12}E_{10}$ increases when sugar concentration is increased.

The various thermodynamic parameters of micellization ($\Delta G_m^0, \Delta H_m^0$ and ΔS_m^0) were evaluated using the phase separation model. The standard free energy of micellization (ΔG_m^0) computed for the systems were negative and became increasingly negative with increasing temperature, which indicate spontaneous micelle formation and spontaneity increases with increasing temperature. In $C_{12}E_{10}$: sugars system, the entropy of micellization ($\Delta S^o{}_m$) were positive, indicating that the micellization process was somewhat entropy-dominated in the absence of sugars. Similar results were observed in $C_{12}E_{10}$: pH system. The enthalpy of micellization is endothermic though it becomes exothermic in the presence of n-alcohols. However the values for EtOH and n-PrOH systems are lower than n-BuOH system. A linear correlation between enthalpy (ΔH_m^0) and entropy of micellization (ΔS_m^0) was observed for all the above surfactant: additive 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. Similar enthalpy-entropy compensation phenomenon was also observed for process of adsorption of surfactants at the air/water interface.

The surface saturation ($\Gamma_{max.}$) increases with increasing temperature for nonionic surfactants. This is due to decreasing hydration of ethoxy segments leading to greater tendency to locate at the air/water interface. The minimum area per molecule of surfactant at the air/water interface ($A_{min.}$) decreases for nonionics with rising temperature whereas, for all the systems low values of $A_{min.}$ (< 1 nm^2)

were obtained. The low $A_{min.}$ values are attributed to closer packing at the air/water interface owing to decreased repulsion between the oriented headgroups in the presence of different additives.

All the ΔG^0_{ad} values were found negative, implying spontaneous adsorption process. However, it is also noteworthy that the ΔG^0_{ad} were always more negative than the corresponding ΔG^0_m values, suggesting that micellization occurs only after the interface becomes saturated with the monomeric surfactant. All the values of entropy of adsorption of surfactants at the air/water interface (ΔS^0_{ad}) 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.

By SANS we observed that at the studied temperature intervals, oblate ellipsoid micelle changed into prolate ellipsoid and the number density of micelles decreased with an increase in the temperature both in the presence and in the absence of sugars and also on increasing the concentration of sugars. In $C_{12}E_{10}$:sugar systems the increase in temperature from 30 to 60°C, the semiminor axis remains almost constant (~26 Å), whereas semimajor axis increased by 2.5-fold and N_{agg} increased by threefold. This indicated a two fold lateral association at 45°C and a three fold association at 60°C. The *axial ratio* and N_{agg} increased when the concentration of D-glucose was increased. It is observed that there is no correlation peak in the low (up to 0.025) Q region, showing the absence of spatial correlation among the nearest neighbors. A rise in temperature results in the dehydration of both the core and corona of the aggregates, and thereby systematically elongating the *semimajor axis* (a), increasing the aggregation number, and even decreases the number density, N_m of the micelle. It was found that our experimental SANS intensity were best matched with the values obtained by using prolate ellipsoidal model in $C_{12}E_9$: amino acid systems. It is also seen that the effect of temperature on size parameters are significant both in absence and presence of amino acids. While the axial ratio as well as N_{agg} are not effected by the concentration of $C_{12}E_9$ change from 5 to 20mM keeping the temperature constant although the number density of micelle increases from 1.9 to 7.8, having axial ratio and N_{agg} almost constant. On increasing the temperature from 30 to 60°C, the *semimajor axis* and the N_{agg} are increased by 70%. This indicates that a lateral elongation of the micelles takes place by including more and more surfactant molecules and hence the N_m decreases. However at the same concentration (0.4M) from *glycine* to *valine* the *axial ratio* is in the range from 2.9 to 3.02, which show that *valine*, is bigger molecule and it occupies more space in micelle. The micelles were found to be ellipsoid at 30°C, however they become rod like with *axial ratio* ~5 both in presence and absence of *amino acids* on increasing the temperature from 30 to 60°C.

It was also observed that the *semimajor axis* registered an increase of 82% with *val* and 70% without *amino acids* with rise in temperature from 30 to 60°C. Accordingly, the *axial ratio* increases substantially. Model fitting of SANS data showed that the surfactant formed prolate ellipsoidal micelle with a constant size (in the concentration range of 5mM to 20mM) but the micelle registered a 60 - 70% increase in size, in the association number and the other micellar parameter (i.e. the number density of micelles changed inversely with the rise in temperature) with rise in temperature from 30 to 60°C. The changes in the parameters have been interpreted mainly in terms of dehydration effects at elevated temperature as observed from the viscosity data.

Dynamic light scattering (DLS) measurements were carried out for $C_{12}E_9$ *amino acid* systems. It is found that on increasing the concentration there is decrease in the diffusion coefficient which indicates that the diffusion of the particles deviates from the normal diffusion and the microstructure of the assemblies in the solution becomes changed. We have also studied the effect of temperature on the hydrodynamic radius and diffusion of $C_{12}E_9$ micelles in the absence and presence of amino acids as we did in SANS and viscosity studies. An increase of temperature favors the breaking of the micelles, and subsequent decrease of the average micellar length was observed. Similar effect was seen in the presence of *valine.* DLS measurements were also carried out for TTAB/Brij-35 mixed surfactant system. The R_h values for mixed system were higher than that of TTAB as well as Brij-35 surfactant. This is because the head group-head group repulsions between the charged TTAB micelles were reduced due to the presence of Brij-35 in the mixed molecule. The R_h values for 16-10-16, $2Br^-$: TX-100 mixed system were found to be higher than that of 16-10-16 $2Br^-$ but lower than TX-100.

Structural and dynamic properties were also elucidated by viscous flow. The intrinsic viscosity $[\eta]$ decreases with increase in temperature, indicating pronounced micellar dehydration. In presence of alcohol similar behavior with respect to temperature was observed. However $|\eta|$ values increase due to more cosolubilization on increasing the concentration as well as on increasing the chain length of alcohols. In presence of amino acids similar behavior with respect to temperature has been observed where the variation is in the order of ala>gly>cys and among the sugars considered, the variation is in the order of: sucrose > D-glucose > D-ribose. From intrinsic viscosity, the hydrated micellar volume (V_h), volume of the hydrocarbon core (V_c) and the volume of the palisade layer of ethylene oxide units (V_{OE}) have been calculated and discussed.

From the slope and the intercepts of the straight line obtained by plotting $\ln(\eta V/Nh)$ against 1/T, the activation enthalpy ($\Delta H^{\#}_{vis}$) and activation entropy ($\Delta S^{\#}_{vis}$) for viscous flow were calculated. $\Delta G^{\#}_{vis}$ was positive in all these systems, indicating a nonspontaneous flow, and it increased with an increase in the concentration of sugars in the order of sucrose > glucose > ribose. $\Delta H^{\#}_{vis}$ value indicated that the viscous flow were endothermic. $\Delta S^{\#}_{vis}$ were positive indicating that the micellar system were not very well structured, either in the absence or in presence of sugars. All alcohols seem to have almost same effect on $\Delta G^{\#}_{vis}$.

We studied the phase diagram of $C_{12}E_9$ and $C_{12}E_{10}$ nonionic surfactants by CP *vs.* concentration plot. The cloud point increases as concentration decreases from dilute to very dilute solution (less than 1%,) in both POE surfactants. However CP decreases as the concentration becomes greater than 1% up to about 10% (w/v). Above 10%(w/v), the CP increases with increasing concentration in the case of $C_{12}E_{10}$. While in $C_{12}E_9$, the CP decreases as the concentration becomes greater than 1% up to about 6% (w/v). Above 8% (w/v) the CP increases with increasing the concentration of surfactant. The decrease in CP with increase in concentration is due to increase in micellar density as we observed in small angle neutron scattering (SANS) study.

Additives have a significant but variable effect (negative or positive) on the CP. There was slight rise in the cloud point (CP) of $C_{12}E_{10}$ by lower alcohols. However a decrease was seen for n-BuOH and n-PenOH. Cloud point of $C_{12}E_{10}$ also decreased in the presence of all three sugars in the order of sucrose> glucose> ribose. The CP of $C_{12}E_9$ (20mM) is found to be 86°C, and it decreases in presence of amino acids in the order of gly>ala>val. It is seen that *p*H have mild effect on cloud point of $C_{12}E_{10}$, it increases only by 2°C by a change of *p*H from 2 to 11. CP of $C_{12}E_{10}$ increases with increase in concentration of tetra butyl ammonium iodide (TBAI) while tetra methyl ammonium bromide (TMAB) decreases. However $Ca(NO_3)_2$ has negligible effect on the CP of $C_{12}E_{10}$. We have also determined the CP of nonionic-nonionic surfactant system: $C_{12}E_9$ and $C_{12}E_{10}$ mixed with Triton X 100 in pure as well as in the presence of NaX and KX. It was observed that the CP of mixed surfactant system at all mole fractions in both the systems was intermediate between either of the pure surfactant.

The ^1H NMR studies of the surfactant solution in presence of alcohols were done. The changes in chemical shifts due to the addition of alcohols were monitored and chemical shifts due to oxyethylene group showed a significant change compared to other peaks in $C_{12}E_{10}$: alcohol systems. There was a small down field chemical shift of OE unit signals, which show that these hydrophilic molecules interact with micelle through intermolecular hydrogen bonding. The main OE signals become broader and spitted when the sugars were added in a 1:1 ratio. The NMR results suggests that the sugars were affecting the hydrophilic group, i.e., OCH_2 CH_2, by interacting with it, probably at the micelle-water interface and that the electronic atmosphere of the OE group at the interface was also affected, but not strongly.

The I_1/I_3 values for all the mixed systems, suggest polar surroundings around pyrene in the micelle interior. We also found, using Maeda's concept, that the chain–chain interactions are very important in these above maintained mixed systems. It is found that the N_{agg} values of the mixed surfactant system are larger than 16–4–16 but lower than $C_{12}E_6$ single surfactant at all mole ratios. The decrease of N_{agg} is obviously associated with the increased average repulsive interaction between head groups with increasing 16–4–16, as nonionic surfactant molecules are progressively replaced by cationic dimeric surfactants. Similar results were obtained in 16-10-16,$2Br^-$:$C_{12}E_6$ surfactant system.

The Krafft temperature (T_k) is the melting point of hydrated surfactant. The T_k of dimeric surfactant were found to increase with the increasing ratio of nonionic monomeric surfactant, as nonionic surfactant makes gemini surfactant less soluble.. Mixture of 16-10-16, $2Br^-$ and TX 100 has less solubility in water than the mixture of 16-10-16, $2Br^-$ and $C_{12}E_6$. This may be due to demicellization of cationic gemini surfactant by TX 100 surfactant. However for 16-10-16, $2Br^-$ / TX 100 mixed system the T_k first increase, then decrease progressively on addition of TX-100. The T_k of TTAB decreases with the increasing ratio of nonionic monomeric surfactant, as the cmc of mixed micelle is lower than that of pure TTAB. The T_k of TTAB decreased as system heterogeneity increases due to addition of Brij-35.

The interaction parameter at mixed micelles (β^m), and at the air – water interfaces (β^σ), indicate an attractive interaction (synergistic behavior) in 16-4-

$16,2Br^-$ /$C_{12}E_6$, 16-10-$16,2Br^-$ /$C_{12}E_6$ and 16-10-$16,2Br^-$ /TX- 100 systems. Recently Maeda suggested that there are chain-chain interactions present in a mixed system in addition to head group-head group interactions given by regular solution approach of Rubingh. Gemini surfactant has a hydrophobic chain of 16 carbons whereas, the nonionic surfactant has 12 and thus contributes to chain-chain interaction. However, the head groups 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 by using Maeda's concept and that of phase separation model were found to be in good agreement.