Abstract

Surfactants form aggregates, particularly in aqueous solutions, via hydrophobic and hydrophilic interactions occurring within the same molecule. These exotic molecules have generated a great deal of interests because of their various industrial applications. While the formation of micelles is the consequence of interplay between hydrophobic and hydrophilic parts of the surfactant molecules with water, it is mainly triggered to avoid loss of entropy due to the formation of ordered water cages around hydrophobic part disrupting the hydrogen bonds between water molecules. There are many factors which influence critical micelle concentration (cmc), size, shape and the aggregation number of ionic micelles. Among these factors, the surfactant head group characteristics, including the counter ion interactions, is perhaps the least studied facet, yet one of the pivotal issues which control the shape and size of the micellar aggregate. Strong binding counter ions favorably influence aggregate formation and decrease the cmc via effective charge screening of the head groups. The formation of an ionic micelle from monomeric ions results in a balance between hydrophobic interactions between the hydrophobic part of the micelle-forming ions, electrostatic interactions between their hydrophilic charged parts, as well as with and between the counterions.

Sodiumdodecylbenzene sulfonate (SDBS) is a well known anionic surfactant widely used in the industry for manufacturing detergents, emulsions, degreaser and deinking agents and also for assisting dying processes in textile factories. Therefore, this work is concerned with dodecylbenzene sulfonate micelles with a view to investigate the effect of a series of alkali metal counterions, such as Li^+, Na^+, K^+ and NH_4^+ on the micellization of DBS. It may be mentioned that the cmc and other thermodynamic parameters of DBS having different counterions have not yet been reported in the literature. Therefore, the present aim is to determine the cmc of DBS with different counterions within the temperature range of 10°C to 40°C and to determine the relevant thermodynamic parameters of micellization, such as ΔG_m^0, ΔH_m^0, ΔS_m^0 and $\Delta_m C_p^0$ along with maximum surface excess concentration ($\Gamma_{\max}$), and the minimum area per molecule (A_{min}) at the surface as a function of hydrated counterion size. Symmetrical tetraalkyl ammonium counter ions with varying alkyl chain length demand special attention because one can study two opposing effects in this series of ions viz., the effect of progressively enhanced hydrophobicity and the effect of increasing dimension of the ions. Counter ion specific

interactions (hydrophobic or hydrophilic) along with change in hydration energy are also very important and this has been discussed in a number of recent reports.

To undertake an in-depth study of the effect of size of the counter ion vis-à-vis its hydrophobicity on the aggregation behaviour of sodiumdodecylbenzene sulfonate, the set of symmetrical tetraalkyl ammonium counter ions with progressively larger groups may be an excellent model which one strives to investigate. This prompted us to synthesize dodecylbenzene sulfonates with tetramethyl, tetraethyl, tetrapropyl and tetrabutyl ammonium counter ions to study their aggregation properties along with the ammonium counter ion.

This thesis contains six chapters. In the first chapter, a general introduction has been given. The second chapter contains the scope and object of the thesis. The third chapter of the thesis presents the result of the effect of alkali metal and organic counterions on the aggregation behaviour of dodecyl benzene sulfonate surfactant. The fourth chapter presents aggregation behaviour of all the surfactants containing alkali metal counter ions and organic counter ions in presence of symmetrical bromide salts and also in presence of an organic additives viz., ethylene glycol. In the fifth chapter, aggregation number has been determined for all the surfactants and dye-surfactant interaction has been studied with an oxazine dye by spectroscopic method. And in the last chapter, effect of cetyltrimethylammonium bromide on the aggregation behaviour of sodium dodecyl benzene sulfonate is presented, since compared to single surfactant, the mixed surfactant exhibits superior interfacial properties such as higher surface activity and lower critical micelle concentration (cmc).

The lithium, potassium and ammonium salts of dodecylbenzene sulfonic acid have been prepared from the pure sodium salt by applying ion-exchange technique. The critical micellization concentrations (cmc) of the surfactants with four different counterions have been determined in a temperature range 10°C to 40°C using surface tension as well as electrical conductivity measurements.

Different tetraalkylammonium viz., $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$, $N^+(C_4H_9)_4$ along with simple ammonium salts of dodecylbenzene sulfonic acid were prepared by ion-exchange technique. The cmcs' of dodecylbenzene sulfonate salts with varied counterions were determined by electrical conductivity and surface tension measurements within the temperature range 283 – 313 K. Counterion ionization constant, α, the surface parameters Γ_{max} and A_{min} and also the thermodynamic parameters of micellization process viz., ΔG_m^0, ΔH_m^0 and ΔS_m^0 in aqueous solution have been determined by using pseudo-phase model. The order of cmc in aqueous solution is found to be $NH_4^+ > N^+(CH_3)_4 > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$ at any given temperature. On the other hand, aggregation number increases with alkyl chain length first due to increasing hydrophobic interactions and then decreases as a function of counterion size passing through a maximum for $N^+(C_2H_5)_4$. Spontaneity of micellization in aqueous solution is supported by large negative ΔG_m^0 as well as the positive entropy change for the micellization process for all the above counterions. At a given temperature, ΔG_m^0 for surfactant with different counterions followed the order $N^+(CH_3)_4 > NH_4^+ > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$. Electrostatic interaction along with effective charge screening and hydrophobicity of the surfactant head group together may give an explanation for the observed variation of aggregation behaviour and the energetics as a function of the nature of counterion.

To study dye-surfactant interaction as influenced by counter ion characteristics, we have taken an oxazine dye (Cresyl fast violet) with dodecylbenzene sulfonate with varying counterions. Due to the dye-surfactant interactions, the changes in spectral characteristics are observed. At concentration below the normal cmc, surfactants and dyes may interact to form a mixed micelle of the two species, lowering the resultant cmc. Above the cmc, a change in the molecular environment of the dye due to incorporation into the micelle interior is observed. The fluorescence spectra of all the surfactant show similar behaviour with the change of surfactant concentrations. The order of the ion pair formation or cluster formation for alkali metal counter ions is as follows: $Li^+ > K^+ > Na^+$ and for tetraalkyl ammonium counter ion along with ammonium ion is as follows: $NH_4^+ > (C_4H_9)_4N^+ > (C_3H_7)_4N^+ > (C_2H_5)_4N^+ > (CH_3)_4N^+$. The trend can be explained as the consequences of the increased charged screening and higher counter ion binding capacity via stronger hydrophobic interactions with the micelles. Anisotropy measurement was done with the same surfactants. The value of the cmc derived from polarization value is in good agreement with the value determined by surface tension and conductometically for each of the surfactant. In the present experiment, time resolved fluorescence studies were carried out to determine the emission decay parameters of all the surfactants with different surfactant concentrations. The concentration of the dye used was 5×10^{-6} (M). The lifetime values did not change significantly or in a regular manner with the change in surfactant concentration suggesting single exponential fluorescence decay curve for all the surfactants.

Mixtures of cationic and anionic surfactants show not only synergistic effect of the aggregation properties but also triggered micellar growth in one dimension to form long worm-like micelles. In the first part, the synergistic effect of the mixing of cetyltrimethylammonium bromide (CTAB, a cationic surfactant) with SDBS (an anionic surfactant) is studied under Newtonian flow regime. In the second part, the formation of viscoelastic worm-like micelles is examined and the rheological behavior of the system is investigated under non Newtonian flow regime. Here the cmc's were determined for the mixed surfactant systems of various mole ratios at a particular temperature. The results indicate that the added cationic surfactant (CTAB in this experiment) is assisting in the micelle formation of the anionic surfactants.

The reason for the non-ideal behaviour among surfactant molecules upon mixing are then various types of molecular interactions. The purely energetic effects usually are much smaller for surfactants mixtures like CTAB and SDBS which explains comparatively lower interactions parameter. When the concentrations of the individual component of the mixtures are increased (e.g., CTAB = 100 mM and SDBS = 20 mM), a viscoelastic gel is formed and the flow becomes non-Newtonian in nature. The observed viscoelasticity is related to worm-like micelle (WLM) formation. No cross over point is displayed beyond the temperature range of 303 K – 313 K, except at 281 K.

The plots for the present system fit to a good extent to a simple Maxwell model particularly at 303 K. The large deviation from Cole – Cole plot with high angular viscosity is indicative that of a less structured system with poor viscoelastic behaviour. From the zero-shear viscosity of the surfactant mixtures, it is clear that with increase in temperature, η_0 increases indicating an increase in the curvature energy for surfactant aggregates which leads to an increase in micellar length and the formation of wormlike micelles. In summary, all these results support a fascinating and complex rheology to exist in the present system is a structural evolution from a spherical micelle to a worm like micelle. Finally, the shift in cross over freequency ω to higher values indicate that the relaxation time τ decreases with temperature.