Role of surfactant-surfactant interactions in mixed micelle solutions

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(Mixed critical micelle concentration (cmc) data have been determined at 303.15 K and 313.15 K by surface tension method for aqueous solutions of sodium dodecylsulphate (SDS) (A) + Triton X-100 (B), and dodecyltrimethylammonium bromide (DTAB) (A) + Triton X-100 (B). The data have been analysed in terms of Rubingh’s approach. The analysis has revealed that surfactant-surfactant interaction energies in the mixed micelles of SDS (A) + Triton X-100 (B) and DTAB (A) + Triton X-100 (B) depend on the bulk mole fraction \(X_A\) of A. The interaction energy data have been rationalized in terms of molecular interactions between the surfactants A and B and the same have been further supported by viscosity data of these binary surfactant systems.

The sharp changes in such physical properties as surface tension, conductance, intensity of scattered light etc., in aqueous solutions of two surfactants have been attributed\(^1\) to the formation of micelles containing both the surfactants in equilibrium\(^2\) with their monomeric species in the aqueous phase. Both critical micelle concentration (cmc) and the distribution of surfactants between the micellar and the aqueous phase play important role\(^2\) in the description of the physical behaviour of binary surfactant solutions in such phenomena as adsorption and solubilization. Although a number of attempts\(^3\)–\(^6\) have been made to describe the dependence of cmc on bulk composition in aqueous solutions of two surfactants, yet all these approaches assume that the mixed micelles are an ideal solution of the two surfactants. While this may be a reasonable approximation when both the surfactants have similar head groups, it would be unrealistic in the case of surfactants having different head groups or belong to different homologous series. For aqueous solution of two surfactants that mix non-ideally, Rubingh\(^1\) has developed an approach that takes due cognizance of surfactant-surfactant interactions within the mixed micelles via the regular solution theory\(^7\). It would, therefore, be of interest to see as to how this approach\(^1\) describes the cmc data of 303.15 and 313.15K, of the aqueous solutions of such surfactant systems as sodium dodecylsulphate (SDS) (A) + Triton X-100 (B), and dodecyltrimethylammonium bromide (DTAB) (A) + Triton X-100 (B).

Materials and Methods

SDS (BDH) was purified by recrystallising it twice from hot ethanol, crystals washed with dry and distilled petroleum ether and dried \textit{in vacuo} over \(P_2O_5\). DTAB (Sigma) and Triton X-100 (sample No. 5548h, Koch-Light, England) were used as such.

For cmc data of pure and the various binary surfactant systems at 303.15K and 313.15 K, stock solutions, of SDS (50 mM), DTAB (50 mM) and Triton X-100 (10 mM) in doubly distilled water were mixed in appropriate proportions to give a series of solutions, which were diluted with doubly distilled water. The surface tension of these solutions were determined by drop weight method using a Stalagmometer described elsewhere\(^8\). The Stalagmometer (filled with the liquid under examination and fitted with a stop cock at one end to control drop formation and attached to a weighed weighing bottle) was placed in an air thermostat maintained at a temperature slightly higher than the working temperature. The entire assembly was then placed in a water thermostat maintained at the working temperature (controlled to within \(\pm 0.01 \) K). After thermal equilibrium, a known number of liquid drops were allowed to fall in the weighing bottle. The process was repeated for a reference liquid of known surface tension and the surface tension of the unknown liquid was calculated by usual method\(^9\). The performance of the Stalagmometer was checked by measuring surface tension of purified benzene, carbon tetrachloride and \(n\)-hexane (all of AR grade) at 303.15 K. The cmcs of the binary surfactant systems were determined from their surface tension versus log (SDS or DTAB cone) plots.

Viscosities of aqueous solutions of the various (A+B) surfactants were measured at 303.15 and 313.15 K as function of the mole fraction \(X_A\) using a modified version of Ubbelohde viscometer\(^9\). The time of flow was measured with a stop watch capable of reading up to 0.01 s. The flow times for the var-
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Eig.l=-Plots of $C^*$ of aqueous solutions of SDS(A) + Triton-100 (B) as a function of mole fraction, $X_A$ of A at (i) 0.303.15 K and (ii) $X$, 313.15 K

Fig. 1—Plots of $C^*$ of aqueous solutions of SDS(A) + Triton-100 (B) as a function of mole fraction, $X_A$ of A at (i) 0.303.15 K and (ii) $X$, 313.15 K

Fig. 2—Plots of $C^*$ of aqueous solution of DTAB(A) + Triton X-100 (B) as a function of mole fraction, $X_A$ of A at (i) 0.303.15 K and (ii) $X$, 313.15 K

ious (A+B) surfactant systems were greater than 320 s at 303.15 and 275 s at 313.15 K and so kinetic corrections were assumed to be negligibly small.

Results
The mixed cmcs ($C^*$) as a function of the mole fraction $X_A$ of surfactant A in aqueous solutions are plotted in Figs 1 and 2. The absolute viscosity data of the aqueous solutions of various (A + B) surfactant systems as a function of $X_A$ are plotted in Figs 3 and 4.

Discussion
We are unaware of any $C^*$ data on the present binary systems with which to compare our results at 303.15 K and 313.15 K. Nevertheless the measured cmc value of SDS (8 mM) and DTAB (15 mM) at 303.15 K compare favourably with the values 8.2 mM$^{0.0}$ and 15 mMM$^{0.1}$ respectively reported for these surfactants at 298.15 K. For Triton X-100 while the measured cmc value at 303.15 is 0.5 mM, a value 0.33 mM$^{2}$ has been reported for it in the literature. Further $C^*$ versus $X_A$ plots at 303.15 K and 313.15 K (Figs 1 and 2) reveal that both these binary surfactant systems yield non-ideal mixed micelles. We envisage that a meaningful insight into these may be obtained if their $C^*$ data are analysed in terms of Rubingh's approach$^1$.

This treatment$^1$ assumes that the surfactants in the mixed micelles do not behave ideally and that their activity coefficients in the mixed micelles can be approximately given$^1$ by regular solution theory. The
The use of phase separation model of micellization and the regular solution approximation results in the development of Eqs (1) and (2).

\[
\frac{x_A^2 \ln [C^*(X_A/C_A x_A)]}{C^*(1 - x_A)} = 1 \quad \ldots (1)
\]

\[
\beta = \ln \left( \frac{C^* X_A/C_A x_A}{1 - x_A} \right) \quad \ldots (2)
\]

These equations relate the cmc (C*) of the mixed micelle with the cmc of pure A (C_A), mole fraction, X_A, of A in the mixed micellar solution, mole fraction, x_A, of A in the mixed micelle and the molar interaction parameter \( \beta \). The parameter \( \beta \) is further defined as

\[
\beta = \frac{(E_{11} + E_{22} - 2E_{12})}{RT} \quad \ldots (3)
\]

where \( E_{11} \) (i = 1 or 2) are the molar energies of interaction between molecules in the pure micelle, and \( E_{12} \) refer to the molar interaction energies between component 1 and 2 in the mixed micelle and the gas constant.

Evaluation of C*, according to this approach, thus requires a knowledge of the parameter \( \beta \). If \( \beta \) be assumed to be independent of the bulk composition, which is highly unlikely, then a single C* datum at X_A can be employed to evaluate x_A from Eq. (1) which can then be utilized to evaluate \( \beta \) for the system from Eq. (2). This value of \( \beta \) can then be employed to evaluate C* at any X_A through Eqs (1) and (2). Alternatively both C* and X_A data for the aqueous solution of the A and B surfactants can be employed to see as to how B changes with X_A. In the present investigation we have employed the experimental C* and X_A data at 303.15 K and 313.15 K to evaluate x_A. From Eq. 1 and hence \( \beta \) from Eq. 2 for SDS (A), DTAB (A) + Triton X-100 (B) system. It is observed that, unlike the constancy of \( \beta \)-values reported by Rubingh, \( \beta \)-values were no longer constant. Thus while \( \beta \) and x_A values for the aqueous binary solutions of SDS (A) + Triton X-100 vary with X_A in accordance with Eqs (4-7),

\[
\beta(303.15 K) = -30.0 + 22.5 \times X_A \quad \ldots (4)
\]

\[
\beta(313.15 K) = -20.0 - 0.7333 \times X_A + 18.3333 \times X_A^2 \quad \ldots (5)
\]

\[
x_A - X_A(303.15 K) = 0.54 - 0.9598 \times X_A + 0.3195 \times X_A^2 \quad \ldots (6)
\]

\[
x_A - X_A(313.15 K) = 0.57 - 1.0216 \times X_A + 21.0 \times X_A^3 \quad \ldots (7)
\]

those for the aqueous binary solutions of DTAB (A) + Triton X-100 (B) these vary with X_A in accordance with Eqs (8-11).

Further, it is interesting to note that while \( \beta \)-values (at 313.15 K) remain constant in the range of 0 < X_A < 0.45, they become progressively more positive in the range of 0.45 < X_A < 1.0 for both these binary surfactant systems. On the other hand while the \( \beta \)-values (at 303.15 K) become progressively more positive with X_A for both these binary surfactant systems, the change is sharper in SDS (A) + Triton X-100 (B) than that in DTAB (A) + Triton X-100 (B) system. Since \( \beta \) (Eq. 3) is a measure of the extent of surfactant (A)-surfactant (B) interactions in the mixed micelles over that of the A-A and B-B interactions in pure micelles, the negative \( \beta \)-values for both the binary surfactant systems suggest that at 303.15 K and 313.15 K the unlike interactions in the mixed micelles predominate over the like interactions in the pure micelles. These interactions evidently are dictated by the relative proportions of A and B in the mixed micelles. At low X_A, appreciably larger cmc of SDS or DTAB (A) as compared to that of Triton X-100 favours the entry of the monomers of A from the bulk solution into the micelles of pure B causing, at the same time, displacement of some of the monomers of B from the micelles of pure B into the bulk solution. The monomers of A then get involved in A-B interactions with the large number of B monomers in the micelles of B. Since the A-B interactions become more pronounced as compared to A-A or B-B interactions in the mixed micelles, \( \beta \) should not only be large and negative but x_A values should also be greater than X_A as has indeed been observed. The \( \beta \) and x_A data as evaluated from Rubingh's approach for the aqueous solutions of SDS or DTAB (A) + Triton X-100 (B) at 303.15 K in the range of 0 < X_A < 0.65 support this viewpoint. Further at low X_A since x_A > X_A and \( \beta \) is large and negative due to preponderance of A-B interactions over A-A or B-B interactions in the mixed micelles, the size of the mixed micelles should become smaller with the increase in X_A. As X_A is increased further, the buildup of Laplace pressure over the curved micellar surface and the close proximity of the charged SDS anions in the mixed micelle would oppose, the entry of the monomers of A from the bulk solution into the micelles of B. At the same time greater hydrophobicity of B as compared to that of A would favour the entry of monomers of B from bulk solution into the

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micelles of pure A so that as $X_A$ is increased further not only should $x_A$ start increasing relatively slowly but $\beta$ values should also start becoming more positive in these binary surfactant systems. The $x_A$ and $\beta$ values at 303.15 K for these surfactant systems lend credence to this view point.

This scheme of molecular interaction in the mixed micelles would then require that at a relatively higher temperature (313.15 K) and low $X_A$, entry of almost the same order of monomers of A from bulk solution into larger sized micelles of B should cause displacement of comparatively smaller number of monomers of B from micelles of B into the bulk solution at 313.15 K than at 303.15 K. This implies that for aqueous solution of SDS or DTAB (A) + Triton X-100 (B) not only should $\beta$ (313.15 K) < $\beta$ (303.15 K) but $\beta$ (313.15 K) values should also remain constant over some $X_A$ values, and $x_A$ (303.15 K) > $x_A$ (313.15 K). In fact the $\beta$-values evaluated at 303.15 and 313.15 K from Rubingh's approach actually follow the sequence: $\beta$ (313.15 K) < $\beta$ (303.15 K), and while $\beta$ at 313.15 K remains constant in the range of $0 < X_A < 0.45$, $x_A$ (313.15 K) < $x_A$ (303.15 K). As $X_A$ is increased further the build-up of Laplace pressure over the mixed micelle surface would not only cause $x_A$ to increase relatively slowly but $\beta$-values would also become more positive. This is found to be so. Again as $x_A > X_A$ in the range of $0 < X_A < 0.5$ and $x_A < X_A$ in the range of $0.6 < X_A < 1.0$ for both these binary surfactant systems at 303.15 K and 313.15 K, the viscosities ($\eta$) of their aqueous binary solutions should be less than their ideal values and $\eta$ (mixture) should be unsymmetrical about $X_A$. The $\eta_{mix}$ versus $X_A$ plots at 303.15 K and 313.15 K for SDS or DTAB (A) + Triton X-100 (B) systems, and $x_{DTAB}$ (303.15 K) > $x_{DTAB}$ (313.15 K) for SDS (A) + Triton X-100 (B) system in the range of $0 < X_{DTAB} < 0.7$ and $x_{DTAB}$ (303.15 K) > $x_{DTAB}$ (313.15 K) in the range of $0.7 < X_{DTAB} < 1.0$ for DTAB(A) + Triton X-100 (B) systems, the present view would require (i) that for SDS (A) + Triton X-100 (B) system the decrease in viscosity ($\Delta \eta$) from the ideal viscosity should be smaller at 313.15 K than that at 303.15 K and (ii) that for DTAB (A) + Triton X-100 (B) system while $\Delta \eta$ (303.15 K) should be > $\Delta \eta$ (313.15 K), in the range of $0.0 < X_{DTAB} < 0.7$, the reverse should be the case in the range of $0.7 < X_A < 1.0$; the $\eta$ versus $X_A$ plot in Figs 3 and 4 support this view point.

The present study has thus, revealed that any successful theory of mixed micellar solution must make appropriate allowance for A-B interactions between the surfactants. Although Rubingh's approach is a significant step in this direction, yet much remains to be done.

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