Surface Adsorption and Micelle Formation of Dodecyltrimethylammonium Chloride and Decylammonium Chloride Mixture

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The surface tension of the aqueous solution of dodecyltrimethylammonium chloride (DTAC) and decylammonium chloride (DeAC) mixture was measured as a function of the total molality and composition of the surfactants at 298.15 K under atmospheric pressure. To make clear the miscibility of surfactants, the compositions in the mixed adsorbed film and micelle were calculated by use of the thermodynamic equations developed previously. The results indicated that both adsorbed film and micelle are richer in DTAC molecules than the bulk solution. Furthermore, the composition in the adsorbed film at the critical micelle concentration (cmc) was evaluated and compared with that in the micelle. It was found that the composition of DeAC in the micelle is smaller than that in the adsorbed film. This forms a striking contrast to the previous observation of dodecylammonium chloride (DAC)-DeAC mixture. It was concluded that the structure and size of polar head group of surfactants have a significant influence on the miscibility of surfactants.

In our previous paper on the subject of the adsorption of dodecylammonium chloride (DAC) and decylammonium chloride (DeAC) mixture from its micellar solution, we have evaluated thermodynamically the compositions of the surfactants in the mixed adsorbed film and micelle.[1] It has been proved that they, though fairly similar with each other, are remarkably different from that in the solution.

Now another combination of surfactants will give us an information about the miscibility of surfactants in the adsorbed film and micelle and make sure of the usefulness of our thermodynamic treatment. In the present study we choose the dodecyltrimethylammonium chloride (DTAC)-DeAC mixture because (i) we have already investigated the adsorption of DTAC from the micellar solution, the effect of *N*-methylation of DAC on the adsorption and micelle formation, and the phase transition of the adsorbed film of DTAC and DeAC mixture at a low concentration,[2-4] (ii) the critical micelle concentration (cmc) of DTAC is smaller than that of DeAC while the surface tension at the cmc is larger, and (iii) an information is expected to be provided about the influence of the chemical structure of polar head group of surfactant on the miscibility.

The surface tension of the aqueous solution of DTAC-DeAC mixture is measured as a function of the total concentration and composition of the mixture at concentrations around the cmc at constant temperature under atmospheric pressure and analyzed by use of the thermodynamic equations advanced by the authors.[1,4,5] Further, the results are compared with those of the DAC-DeAC system.

Experimental

Dodecyltrimethylammonium chloride and decylammonium chloride were synthesized and purified by the method described previously.[6,7] Water was distilled triply, the second and third stages being from dilute alkaline permanganate solution. Surface tension was measured under atmospheric pressure at 298.15 K by the drop volume method described in the previous paper.[8] The surface tension values were reproducible to ±0.05 mN m^{-1}.

Results and Discussion

To obtain the compositions in the adsorbed film and micelle in equilibrium with the aqueous solution of surfactant mixture, the total molality m of surfactants in the solution defined by

$$m = m_1 + m_2 \qquad (1)$$

and the composition of the surfactant 2 in the total surfactant defined by

$$X_2 = m_2/m \qquad (2)$$

were adopted as the experimental variables at constant temperature and pressure.[1,4,5] Here m_i is the molality of surfactant i.

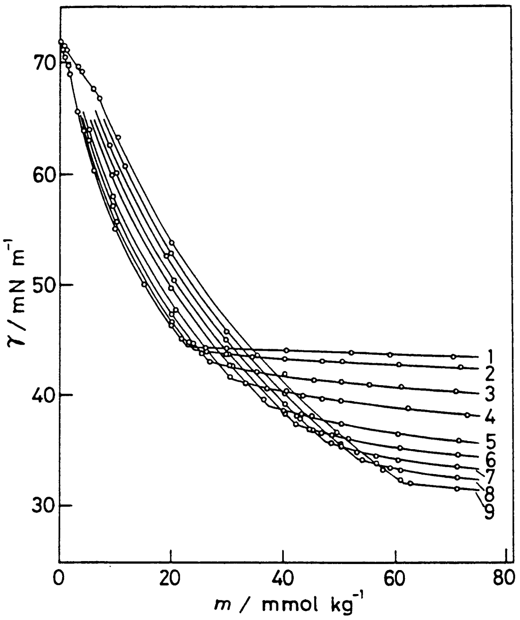

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) X_2=0; (2) 0.1000; (3) 0.3017; (4) 0.5002; (5) 0.7021; (6) 0.8026; (7) 0.8932; (8) 0.9506; (9) 1.

The surface tension of the aqueous solution of dodecyltrimethylammonium chloride and decylammonium chloride mixture was measured as a function of m at fixed composition X_2 of DeAC and at 298.15 K under atmospheric pressure. The results are shown in Fig. 1. It is seen that the γ vs. m curve changes its shape gradually with X_2 from the curve of DTAC to that of DeAC. The curve has a distinct break point arising from the formation of micelles; the concentration at the break point is referred to as the critical micelle concentration (cmc). The cmc value increases with increasing X_2 and the surface tension at the cmc γ^{cmc} decreases. Here, it should be noted that the slope of γ vs. m curve of the micellar solution of mixture has a larger absolute value than those of pure DTAC and DeAC.

Taking up the γ values at a given m value from Fig. 1, the γ vs. X_2 curves are obtained and shown in Fig. 2 together with the γ^{cmc} vs. X_2 curve. It is seen that the value of γ increases with increasing X_2 while that of γ^{cmc} decreases. On the other hand, the m vs. X_2 curves at a given surface tension obtained from Fig. 1 are shown in Fig. 3 with the cmc vs. X_2 curve. It is found that both values of m and cmc increase with X_2.

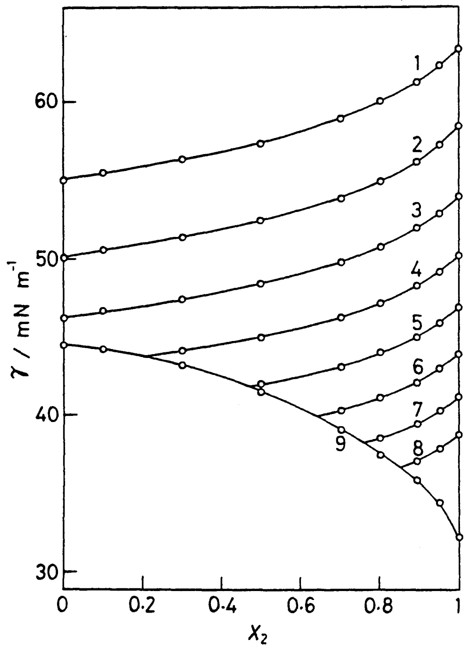

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) m=10 mmol kg^{-1}; (2) 15; (3) 20; (4) 25; (5) 30; (6) 35; (7) 40; (8) 45; (9) γ^{cmc} vs. X_2.

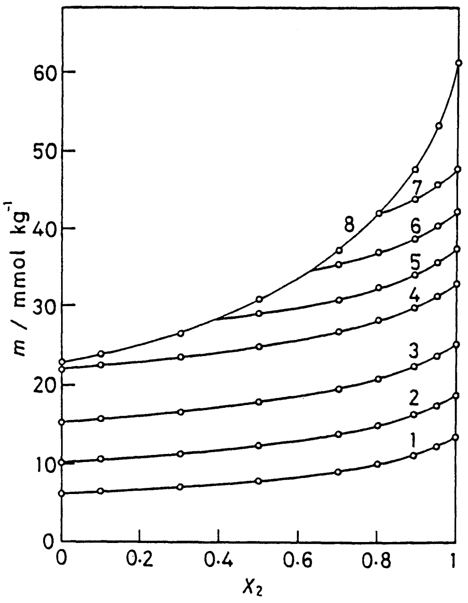

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) γ=60 mN m^{-1}; (2) 55; (3) 50; (4) 45; (5) 42.5; (6) 40; (7) 37.5; (8) cmc vs. X_2.

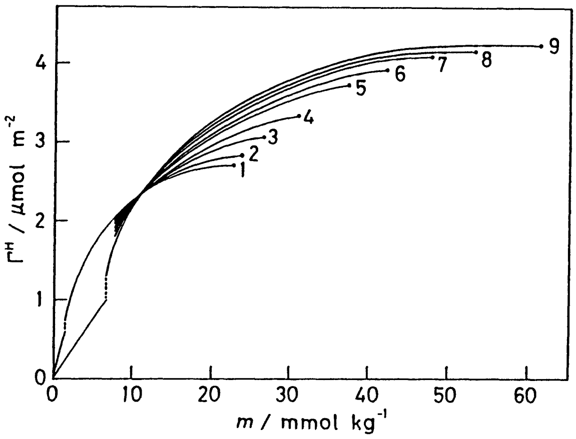

Fig. 4. Total surface density vs. total molality curves at constant composition: (1) X_2=0; (2) 0.1000; (3) 0.3017; (4) 0.5002; (5) 0.7021; (6) 0.8026; (7) 0.8932; (8) 0.9506; (9) 1; (●) total surface density at the cmc $\Gamma^{\mathrm{H,cmc}}$.

Now let us evaluate the total surface density of surfactant mixture Γ^{H} defined by

$$\Gamma^{\mathrm{H}}=\Gamma_1^{\mathrm{H}}+\Gamma_2^{\mathrm{H}}, \qquad (3)$$

where Γ_i^{H} is the surface excess number of moles per unit area of surfactant i with respect to the two dividing planes chosen so as to make the surface excess numbers of moles of water and air zero. Assuming that the solution is ideal, the total surface density is calculated by use of the equation

$$\Gamma^{\mathrm{H}}=-(m/2RT)(\partial\gamma/\partial m)_{T,p,X_2}, \qquad (4)$$

where T is the temperature, p the pressure, and R the gas constant. The evaluated values of Γ^{H} are plotted against m at various compositions in Fig. 4. It should be noted that the value of Γ^{H} increases with decreasing the composition at low concentrations, while it decreases at high concentrations. Taking into account that the DTAC molecule has a larger head group than the DeAC molecule, the large size of the polar head group of DTAC molecule is said to reduce considerably the adsorption of surfactants at a high surface density even though the DTAC molecule has a longer hydrocarbon chain.

It has been shown that the plots of γ at constant m and of m at constant γ against the composition of DeAC in the adsorbed film X_2^H provide us the useful information to examine the miscibility of surfactants in the mixed adsorbed film. Here the composition X_2^H is defined by

$$X_2^H = \Gamma_2^H / \Gamma^H. \tag{5}$$

The values of X_2^H at constant m are calculated by applying the relation

$$X_2^H = X_2 - [(1-X_2)X_2/RT\Gamma^H](\partial\gamma/\partial X_2)_{T,p,m} \tag{6}$$

to the γ vs. X_2 curves given in Fig. 2 with the Γ^H values of Fig. 4 and those at constant γ by applying the relation

$$X_2^H = X_2 - [2(1-X_2)X_2/m](\partial m/\partial X_2)_{T,p,\gamma} \tag{7}$$

to the m vs. X_2 curves given in Fig. 3.[1,4] Both results are respectively shown in Figs. 5 and 6. These diagrams take the shape of cigar and are similar to the three-dimensional phase diagram of an ideal system. Therefore we can say that the DTAC and DeAC molecules are perfectly miscible in the adsorbed film. It is also seen that the adsorbed film is richer in DTAC molecules. This implies that the mixed adsorbed film abounds in the surfactant having a lower surface tension at a given concentration. Further the qualitative feature of the diagram is almost the same as that of the DAC-DeAC mixture.[1] However, the diagrams in Fig. 5 seem to be thinner than the corresponding ones of the DAC-DeAC mixture. This is visualized by plotting the difference in composition between the solution and the adsorbed film $X_2 - X_2^H$ against X_2 (Fig. 7); the differences of the DTAC-DeAC mixture are much smaller than those of the DAC-DeAC mixture both at a given γ and at a given m. Taking into account that the DTAC and DAC molecules are different only in the structure and size of the polar head group, it is concluded that the large head group of DTAC increases the composition of DeAC and decreases the total surface density remarkably at high concentrations.

Next, let us discuss the miscibility of the surfactants in the mixed micelle. We define the thermodynamic quantity of micelle as the excess one in reference to the spherical dividing surface which makes the excess number of moles of water zero[5] and the composition of DeAC in the mixed micelle X_2^M as

$$X_2^M = N_2^M / (N_1^M + N_2^M), \tag{8}$$

where N_i^M is the number of surfactant i in the micelle particle. The value of X_2^M is calculated by application of the relation[1,5]

$$X_2^M = X_2 - [2(1-X_2)X_2/\mathrm{cmc}](\partial \mathrm{cmc}/\partial X_2)_{T,p} \tag{9}$$

to the cmc vs. X_2 curve given in Fig. 3. The cmc vs. X_2^M

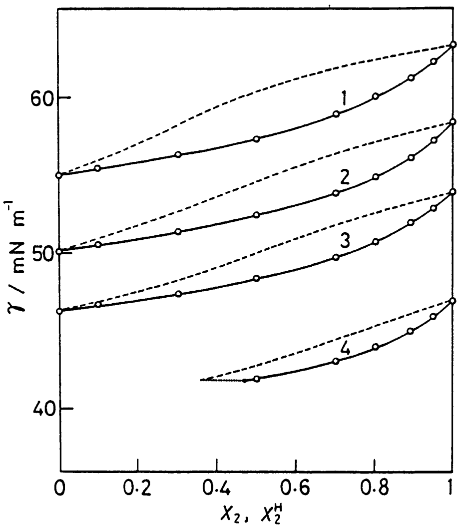

Fig. 5. Surface tension vs. composition curves at constant total molality; (1) m=10 mmol kg^{-1}; (2) 15; (3) 20; (4) 30; (●) γ^{cmc}; (——) X_2; (----) X_2^H.

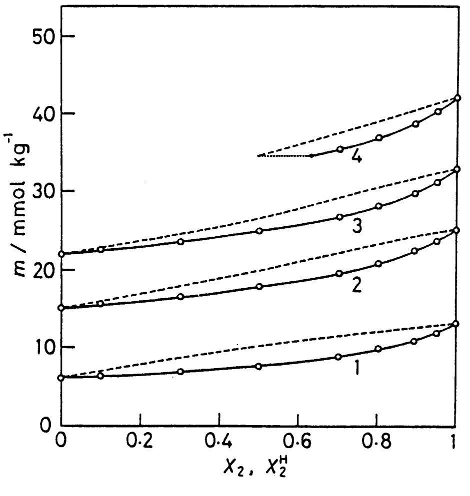

Fig. 6. Total molality vs. composition curves at constant surface tension: (1) γ=60 mN m^{-1}; (2) 50; (3) 45; (4) 40; (●) cmc; (——) X_2; (----) X_2^H.

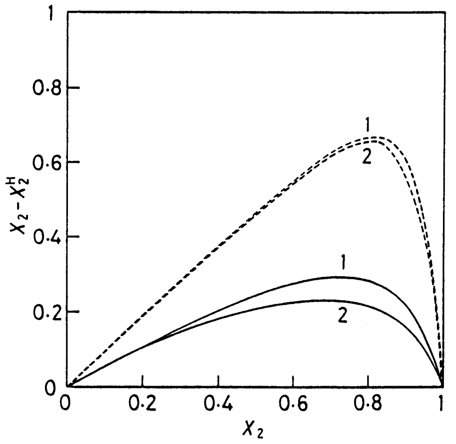

Fig. 7. Difference in composition between the solution and the adsorbed film vs. composition curves at constant molality and constant surface tension: (1) m=14 mmol kg^{-1}; (2) γ=50 mN m^{-1}; (——) DTAC-DeAC system; (----) DAC-DeAC system.

curve is depicted together with the cmc vs. X_2 curve in Fig. 8. It is seen that the diagram has the shape of a swollen cigar and the micelle is richer in DTAC molecules than the solution. Since the mixed adsorbed film is in equilibrium with the bulk solution containing the micelles at a concentration above the cmc, it is useful to compare the compositions in the micelle and adsorbed film. The composition in the adsorbed film at the cmc $X_2^{\mathrm{H,cmc}}$ is obtained by virtue of the equation

$$X_2^{\mathrm{H,cmc}} = X_2^{\mathrm{M}} - [(1-X_2)X_2/RT\Gamma^{\mathrm{H,cmc}}]\,(\partial\gamma^{\mathrm{cmc}}/\partial X_2)_{T,p}, \quad (10)$$

where $\Gamma^{\mathrm{H,cmc}}$ is the total surface density at the cmc.[1] By applying this equation to the γ^{cmc} vs. X_2 curve given in Fig. 2 and using the X_2^{M} value in Fig. 8, the values of $X_2^{\mathrm{H,cmc}}$ were evaluated; the results are also depicted in the form of the cmc vs. $X_2^{\mathrm{H,cmc}}$ curve in Fig. 8. We can see that the adsorbed film at the cmc is also richer in DTAC molecules than the bulk solution. However, it is noteworthy that the composition of DeAC in the adsorbed film is larger than that in the micelle. This behavior forms a striking contrast to that of the DAC-DeAC system.[1]

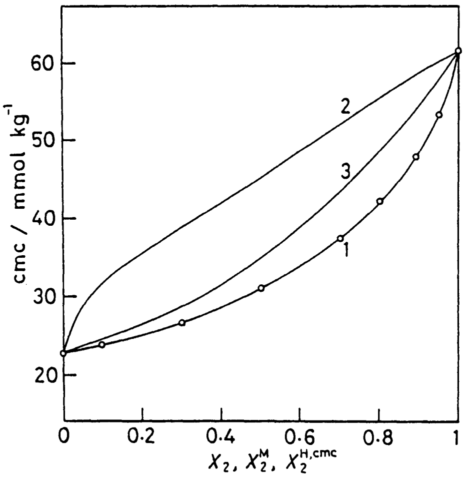

Fig. 8. Critical micelle concentration vs. composition curves: (1) cmc vs. X_2; (2) cmc vs. X_2^{M}; (3) cmc vs. $X_2^{\mathrm{H,cmc}}$.

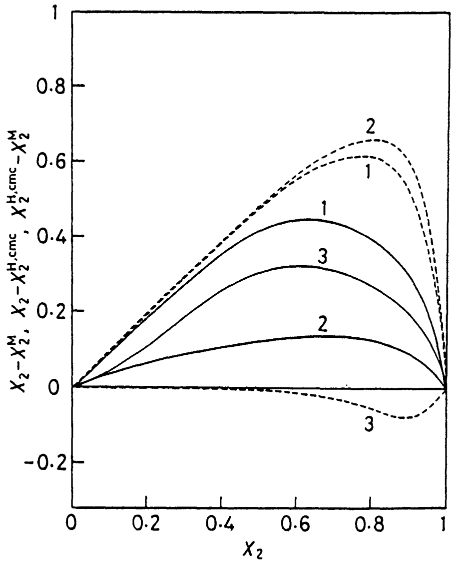

Fig. 9. Difference in composition vs. composition curves at the cmc: (1) $X_2-X_2^{\mathrm{M}}$ vs. X_2; (2) $X_2-X_2^{\mathrm{H,cmc}}$ vs. X_2; (3) $X_2^{\mathrm{H,cmc}}-X_2^{\mathrm{M}}$ vs. X_2; (——) DTAC-DeAC system; (----) DAC-DeAC system.

Now let us consider the values of $X_2-X_2^{\mathrm{M}}$, $X_2-X_2^{\mathrm{H,cmc}}$, and $X_2^{\mathrm{H,cmc}}-X_2^{\mathrm{M}}$ to elucidate the relation among the compositions in the bulk, surface, and micelle. They are plotted against X_2 in Fig. 9. It is clearly seen that the $X_2-X_2^{\mathrm{M}}$ value is considerably large compared with the $X_2-X_2^{\mathrm{H,cmc}}$ value. However, on looking at the corresponding ones of the DAC-DeAC system depicted also in Fig. 9, we notice that the $X_2-X_2^{\mathrm{M}}$ and the $X_2-X_2^{\mathrm{H,cmc}}$ values are not so different than each other. This fact indicates that the difference in composition between the adsorbed film and micelle stems from that in geometrical shape when the polar head groups of surfactants are different in shape and size. Furthermore, taking into account that the $X_2-X_2^{\mathrm{H,cmc}}$ values of the two systems are fairly different though the $X_2-X_2^{\mathrm{M}}$ values are relatively close to each other, it is concluded that the miscibility in the adsorbed film is influenced more significantly by the structure of polar head group than that in the micelle. A similar conclusion has been drawn from the effect of the *N*-methylation of dodecylammonium chloride on the entropies of interface and micelle formation.[3] There is one more important difference between the two systems; that is, the value of $X_2^{\mathrm{H,cmc}}-X_2^{\mathrm{M}}$ is positive for the present system, while negative for the DAC-DeAC system. We can say therefore that the bigger head group is favorable to the micelle formation.

Finally, it is possible to show that the γ^{cmc} vs. composition diagram is helpful to understand the variation of the surface tension of surfactant mixture in the range of concentration above the cmc. It is seen from Fig. 10 that as the total molality m of surfactant mixture increases at a given overall composition X_2, the composition X_2^{M} in the mixed micelle increases and

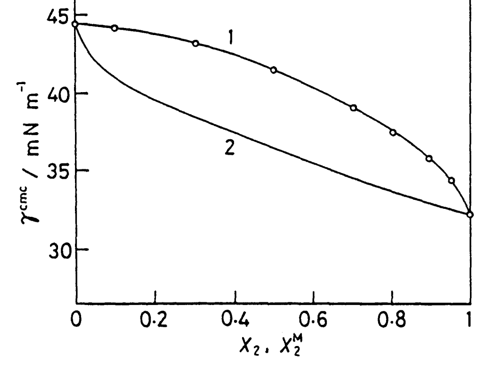

Fig. 10. Surface tension at the cmc vs. composition curves: (1) γ^{cmc} vs. X_2; (2) γ^{cmc} vs. X_2^{M}.

approaches X_2 at an infinite m. Consequently the surface tension of the micellar solution of mixture is expected to decrease gradually with increasing m. Inspecting Fig. 1, the γ vs. m curve of mixture is found to have a larger negative slope than those of pure DTAC and DeAC at concentrations above the cmc. This is consistent with the above expectation.

References

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