August, 1989] *Bull. Chem. Soc. Jpn.*, **62**, *2507—2511 (1989)* 2507

Adsorption at Water/Air Interface and Micelle Formation of Decylammonium Bromide and Decylammonium Chloride Mixture

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(Received April 12, 1989)

The surface tension of the aqueous solution of decylammonium bromide (DeAB) and decylammonium chloride (DeAC) mixture was measured as a function of the total molality and composition of surfactants at 298.15 K under atmospheric pressure. By applying the thermodynamic equations derived previously to the experimental results, the compositions in the mixed adsorbed film and mixed micelle were evaluated. It was found that the adsorbed film and micelle are rich in DeAB, which is more surface active than DeAC, compared with the aqueous solution. Further, the DeAB and DeAC molecules were concluded to mix ideally in the states of the adsorbed film and micelle. On the other hand, the compositions were compared with those of dodecylammonium chloride (DAC)-DeAC mixture at the critical micelle concentration (cmc). The discrepancy between the compositions was proved to be related closely to the differences between the cmc's and between the surface tension values at the cmc of pure surfactants.

The miscibility of surfactants in adsorbed films and micelles has been clarified thermodynamically by use of the excess thermodynamic quantities defined with reference to dividing planes and the two-dimensional phase diagrams representing the relation between the compositions of surfactants in the aqueous solution, adsorbed film, and micelle.[1-5] In the previous paper, the adsorbed film and micelle of dodecylammonium chloride (DAC)-decylammonium chloride (DeAC) mixture have been investigated by measuring the surface tension of the aqueous solution;[1,4] the difference of the surfactant ions has been shown to produce a considerable effect on the adsorption and micelle formation.

It is now important to examine the miscibility of surfactants having different counter ions in the adsorbed films and micelles, because the densities of aqueous solutions,[6-9] the micelle aggregation numbers,[10] and the surface activities[11,12] of surfactants are greatly dependent on the counter ion. In the present study, we adopt the decylammonium bromide (DeAB)-DeAC mixture. The surface tension of the aqueous solution is measured as a function of the total concentration and composition of the surfactants in the neighborhood of the critical micelle concentration (cmc) at constant temperature under atmospheric pressure. The results are compared with those of the DAC-DeAC system at the cmc.

Experimental

Decylammonium bromide was prepared from decylamine (Tokyo Kasei's guaranteed reagent) and hydrobromic acid (Nacalai Tesque's guaranteed reagent) and recrystallized five times from ethanol. Decylammonium chloride was prepared and purified by the method described previously.[1] The purity of the surfactants was checked by observing the absence of a minimum on the surface tension vs. concentration curves. Water was triply distilled from dilute alkaline permanganate solution.

The surface tension of aqueous solutions was measured by the drop volume technique described previously.[13] The error estimated for the value of surface tension was less than 0.05 $\mathrm{mN\,m^{-1}}$. The measurements were carried out at the temperature kept constant at 298.15 K by immersing the cell in a thermostat under atmospheric pressure.

Results and Discussion

It has been shown that the total molality and composition of a surfactant mixture in the aqueous solution are appropriate for the variables to provide information concerning the adsorption behavior and micelle formation of the mixture at constant temperature T and pressure p.[1-5] Here the total molality and composition are defined respectively by

$$m = m_1 + m_2 \tag{1}$$

and

$$X_2 = m_2/m, \tag{2}$$

where m_i is the molality of surfactant i and the component 2 refers to DeAC. The surface tension γ was measured as a function of m at several X_2 values at 298.15 K under atmospheric pressure.

Figure 1 shows the variation in γ with m. It is seen

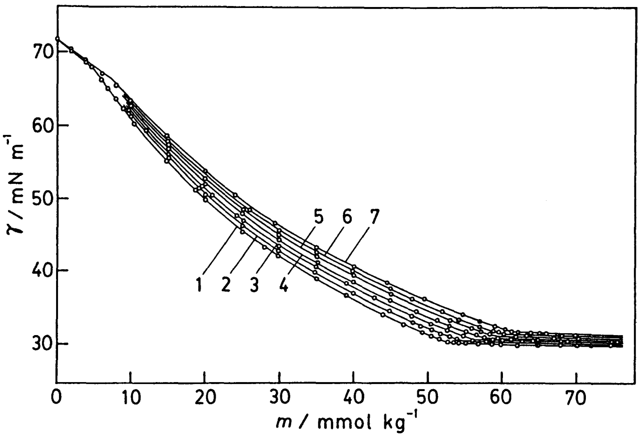

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) X_2=0; (2) 0.299; (3) 0.500; (4) 0.650; (5) 0.800; (6) 0.900; (7) 1.

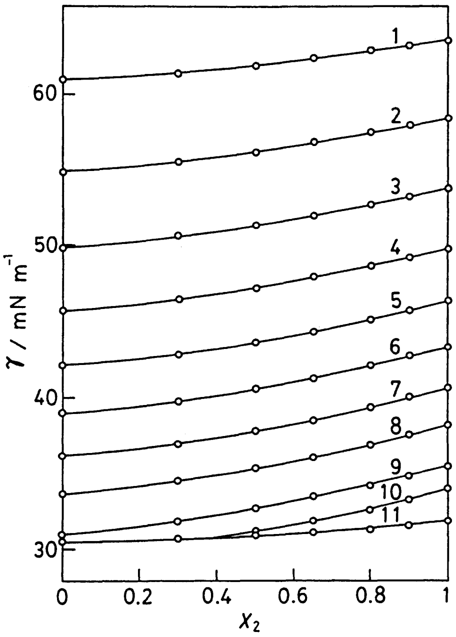

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) m=10 mmol kg^{-1}; (2) 15; (3) 20; (4) 25; (5) 30; (6) 35; (7) 40; (8) 45; (9) 51; (10) 55; (11) γ^{cmc} vs. X_2.

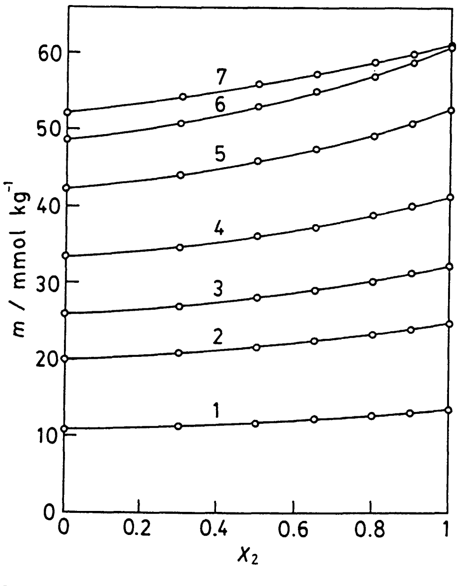

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) γ=60 mN m^{-1}; (2) 50; (3) 45; (4) 40; (5) 35; (6) 32; (7) cmc vs. X_2.

that the value of γ decreases with increasing m and in the range of concentration above the cmc it does slightly and linearly. Further, the curve seems to have a distinct break point at the concentration corresponding to the cmc. By picking up the γ values at a concentration below the cmc from Fig. 1, the γ vs. X_2 curve is obtained and depicted together with the surface tension at the cmc γ^{cmc} vs. X_2 curve in Fig. 2. It is seen that the curves deviate slightly downward from the straight line connecting the γ values of pure DeAB and DeAC. Further, the m vs. X_2 curve at constant γ can also be obtained from Fig. 1; it is shown together with the cmc vs. X_2 curve in Fig. 3. We can find that the shape of the curve is convex downward at a low surface tension value though linear at a high one.

Let us first deal with the adsorption behavior of the surfactant mixture. According to the thermodynamics of adsorption of ionic surfactant mixtures developed previously,[1,2] the surface tension can be written as a function of m and X_2 at a concentration below the cmc at constant T and p:

$$d\gamma = -2(RT\Gamma^{H}/m)dm - [RT\Gamma^{H}(X_2^{H}-X_2)/X_1X_2]dX_2, \quad (3)$$

where the total surface density of surfactants Γ^H and the composition of DeAC in the mixed adsorbed film X_2^H are defined respectively by

$$\Gamma^{H} = \Gamma_1^{H} + \Gamma_2^{H} \quad (4)$$

and

$$X_2^{H} = \Gamma_2^{H}/\Gamma^{H} \quad (5)$$

Here Γ_i^H is the surface excess number of moles of surfactant i with reference to the two dividing planes making the surface excess numbers of moles of air and water zero.[14,15]

The value of Γ^H is evaluated by applying the following equation derived from Eq. 3 to the γ vs. m curve given in Fig. 1:

$$\Gamma^{H} = -(m/2RT)(\partial\gamma/\partial m)_{T,p,X_2}. \quad (6)$$

The Γ^H value is plotted against m at constant X_2 in Fig. 4; it is observed to increase with increasing m and approach the saturated value at a concentration near the cmc. It should be noted that the discontinuous change in Γ^H at a low concentration corresponds to the phase transition in the adsorbed film.[16]

It is apparent from Eq. 3 that there are two approaches to the evaluation of the composition in

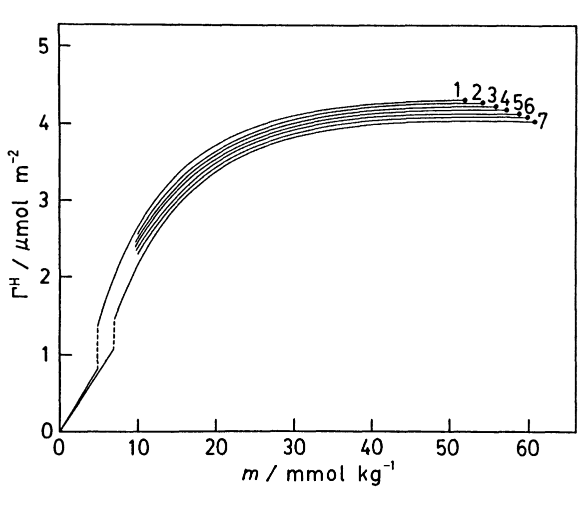

Fig. 4. Total surface density vs. total molality curves at constant composition: (1) X_2=0; (2) 0.299; (3) 0.500; (4) 0.650; (5) 0.800; (6) 0.900; (7) 1; (●) total surface density at the cmc $\Gamma^{H,cmc}$.

the mixed adsorbed film; one is the application of the equation

$$X_2^{\rm H} = X_2 - (X_1X_2/RT\Gamma^{\rm H})(\partial\gamma/\partial X_2)_{T,p,m} \tag{7}$$

to the γ vs. X_2 curve at constant T, p, and m shown in Fig. 2 and the other is the application of the equation

$$X_2^{\rm H} = X_2 - 2(X_1X_2/m)(\partial m/\partial X_2)_{T,p,\gamma} \tag{8}$$

to the m vs. X_2 curve at constant T, p, and γ shown in Fig. 3. The $X_2^{\rm H}$ values are presented in the forms of γ vs. $X_2^{\rm H}$ and m vs. $X_2^{\rm H}$ curves respectively in Figs. 5 and 6, where the corresponding γ vs. X_2 and m vs. X_2 curves are also depicted. It is seen that the value of $X_2^{\rm H}$ is smaller than that of X_2; that is, the mixed adsorbed film is enriched with DeAB, which has a smaller γ value than DeAC, over the whole range of composition. Taking account of the difference in chemical structure between DeAB and DeAC, the counter ion is said to have some effect on the adsorption behavior of surfactant ion. However, it is found that the composition difference $X_2-X_2^{\rm H}$ is small compared with that of the DAC-DeAC system which is characterized by the different surfactant ion and the same counter ion.[1,4] Furthermore, the m vs. $X_2^{\rm H}$ curve seems not to deviate appreciably from the line connecting the m values of the pure surfactants. These findings indicate that the DeAB and DeAC molecules mix almost ideally in the adsorbed film.

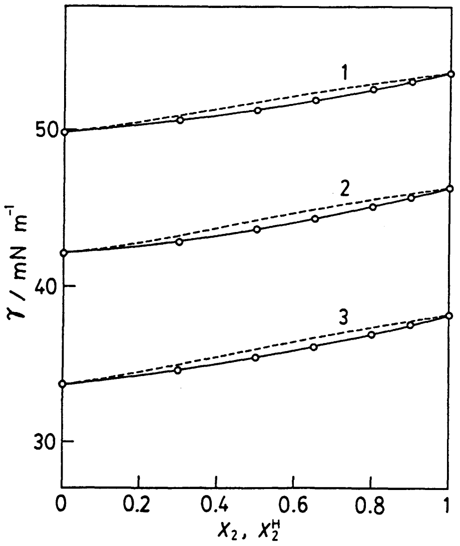

Fig. 5. Surface tension vs. composition curves at constant total molality: (1) m=20 mmol kg^{-1}; (2) 30; (3) 45; (——) X_2; (----) $X_2^{\rm H}$.

Now let us consider the mixed micelle formation of surfactants. The thermodynamic equation describing the behavior of the mixed micelle at the cmc at constant T and p is[3]

$$-2(RT/{\rm cmc}){\rm dcmc} - [RT(X_2^{\rm M}-X_2)/X_1X_2]{\rm d}X_2 = 0, \tag{9}$$

where $X_2^{\rm M}$ is the composition of DeAC in the mixed micelle defined by

$$X_2^{\rm M} = N_2^{\rm M}/(N_1^{\rm M}+N_2^{\rm M}), \tag{10}$$

where $N_i^{\rm M}$ is the number of molecules of surfactant i in one mixed micelle particle defined with regard to the spherical dividing surface which makes the excess number of moles of water zero. From Eq. 9, we can derive the relation between $X_2^{\rm M}$ and the derivative of the cmc with respect to X_2:

$$X_2^{\rm M} = X_2 - 2(X_1X_2/{\rm cmc})(\partial{\rm cmc}/\partial X_2)_{T,p}. \tag{11}$$

The $X_2^{\rm M}$ value obtained from the cmc vs. X_2 curve shown in Fig. 3 is expressed in the form of the cmc vs. $X_2^{\rm M}$ curve in Fig. 7, where the cmc vs. X_2 curve is also drawn. It is seen that the population of DeAC in the mixed micelle is smaller than that in the solution although the difference between them is small. Sim-

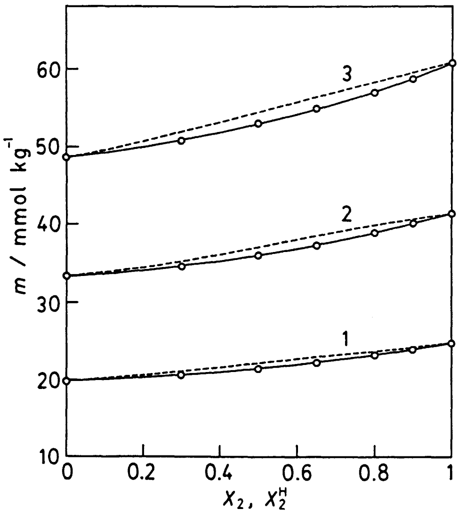

Fig. 6. Total molality vs. composition curves at constant surface tension: (1) γ=50 mN m^{-1}; (2) 40; (3) 32; (——) X_2; (----) $X_2^{\rm H}$.

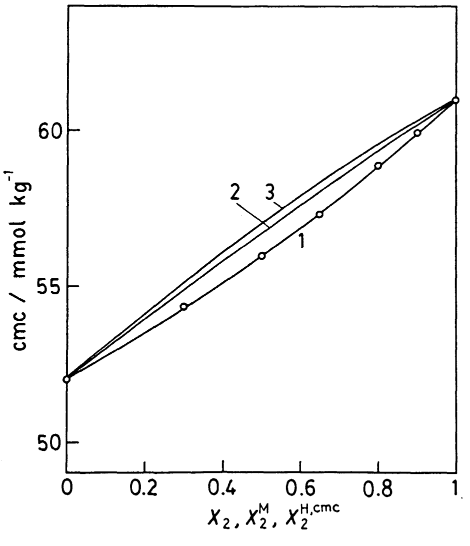

Fig. 7. Critical micelle concentration vs. composition curves: (1) cmc vs. X_2; (2) cmc vs. $X_2^{\rm M}$; (3) cmc vs. $X_2^{\rm H,cmc}$.

ilar behavior was observed in the case of the potassium dodecyl sulfate-sodium dodecyl sulfate system.[3] Therefore, we may say that the DeAB and DeAC molecules mix ideally in the micelle as those in the adsorbed film.

Further, the X_2^{H} value at the cmc $X_2^{\mathrm{H,cmc}}$ can be calculated by use of the composition dependence of the γ^{cmc} shown in Fig. 2 and the relation

$$X_2^{\mathrm{H,cmc}} = X_2^{\mathrm{M}} - (X_1X_2/RT\Gamma^{\mathrm{H,cmc}})(\partial\gamma^{\mathrm{cmc}}/\partial X_2)_{T,p}, \qquad (12)$$

which is derived by combining Eq. 3 at the cmc with Eq. 9. Here $\Gamma^{\mathrm{H,cmc}}$ is the total surface density of surfactants at the cmc represented by the closed circle in Fig. 4. The value of $X_2^{\mathrm{H,cmc}}$ is shown in the form of the γ^{cmc}vs. $X_2^{\mathrm{H,cmc}}$ plot in Fig. 8 and also in the form of the cmc vs. $X_2^{\mathrm{H,cmc}}$ plot in Fig. 7. Comparing the values of $X_2^{\mathrm{H,cmc}}$ and X_2^{M}, we notice that the micelle is slightly rich in DeAC compared with the adsorbed film. Since the difference between the values are small, however, it may be concluded that the miscibility of surfactants in the micelle is similar to that in the adsorbed film. This fact gives support to our view that the behavior of surfactants in the micelle resembles thermodynamically that in the adsorbed film.[4,17]

Finally, it is useful to compare the relation between the compositions in the aqueous solution, adsorbed film, and micelle of the DeAB-DeAC mixture with that of the DAC-DeAC mixture at the cmc. The cmc vs. composition curves are drawn in Fig. 9. It is clearly seen that the diagram of the DeAB-DeAC system is extremely thin compared with that of the DAC-DeAC system. To visualize the difference between the two systems quantitatively, the $X_2-X_2^{\mathrm{M}}$, $X_2-X_2^{\mathrm{H,cmc}}$, and $X_2^{\mathrm{H,cmc}}-X_2^{\mathrm{M}}$ values are plotted against X_2 in Fig. 10. Both the adsorbed film and the micelle are seen to be enriched with the surfactant which has the lower γ^{cmc} and cmc values. However, the $X_2-X_2^{\mathrm{M}}$ and $X_2-X_2^{\mathrm{H,cmc}}$ values of the DeAB-DeAC mixture are much smaller than those of the DAC-DeAC mixture; this may be attributable to a small difference in cmc between the constituents of the former mixture. On the other hand, the $X_2^{\mathrm{H,cmc}}-X_2^{\mathrm{M}}$ values of both the mixtures seem not to be different from each other, which arises from the fact that their differences in γ^{cmc}

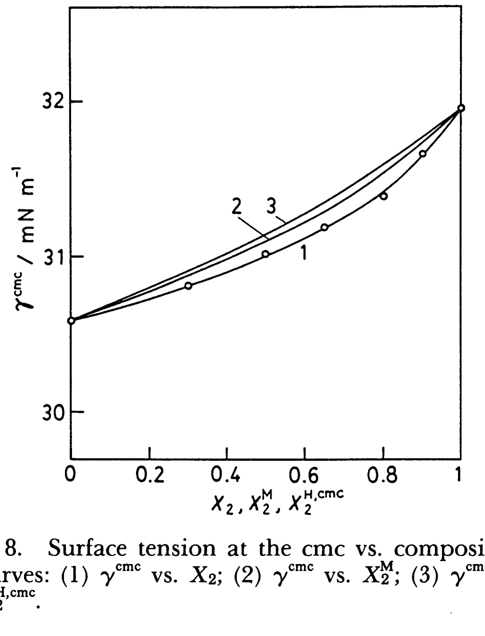

Fig. 8. Surface tension at the cmc vs. composition curves: (1) γ^{cmc} vs. X_2; (2) γ^{cmc} vs. X_2^{M}; (3) γ^{cmc} vs. $X_2^{\mathrm{H,cmc}}$.

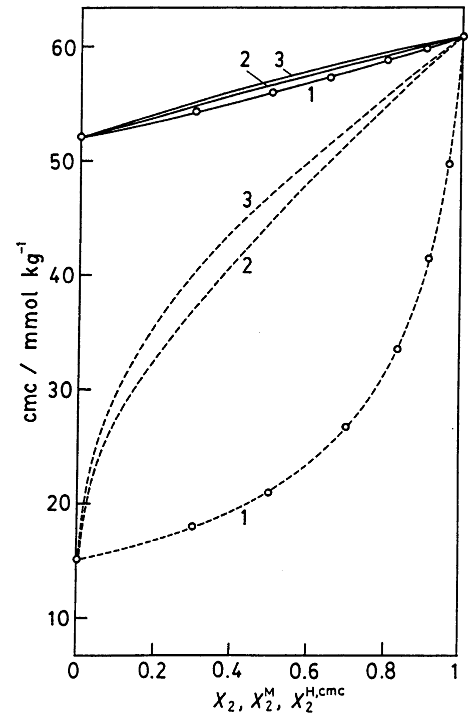

Fig. 9. Critical micelle concentration vs. composition curves: (1) cmc vs. X_2; (2) cmc vs. X_2^{M}; (3) cmc vs. $X_2^{\mathrm{H,cmc}}$; (——) DeAB-DeAC system; (----) DAC-DeAC system.

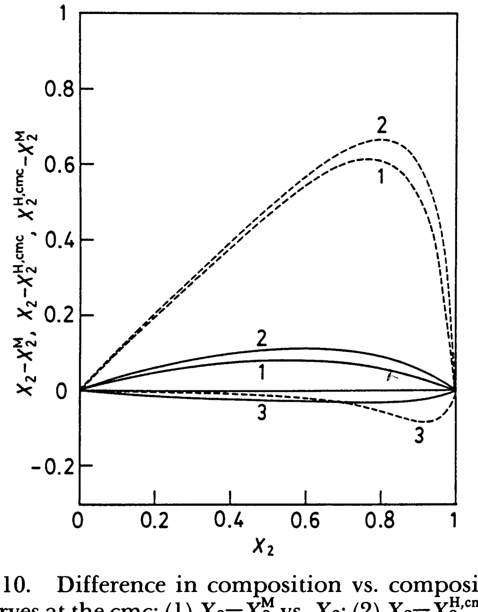

Fig. 10. Difference in composition vs. composition curves at the cmc: (1) $X_2-X_2^{\mathrm{M}}$ vs. X_2; (2) $X_2-X_2^{\mathrm{H,cmc}}$ vs. X_2; (3) $X_2^{\mathrm{H,cmc}}-X_2^{\mathrm{M}}$ vs. X_2; (——) DeAB-DeAC system; (----) DAC-DeAC system.

between the constituents are comparable.

Further information about the miscibility of surfactants in the adsorbed film and micelle will be provided by examining the mixture of surfactants without a common ion.

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