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

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The miscibility of dodecyltrimethylammonium chloride (DTAC) and dodecylammonium chloride (DAC) in the adsorbed film at water/air interface and in the micelle was investigated by measuring the surface tension of the aqueous solution of surfactant mixture as a function of the total molality and composition of surfactants. The compositions of surfactants in the adsorbed film and micelle were evaluated by use of the thermodynamic equations developed previously. The results indicated that DTAC and DAC molecules mix slightly nonideally in the adsorbed film and micelle. Furthermore, the composition of DAC in the micelle was found to be remarkably smaller than that in the adsorbed film at the critical micelle concentration. It was concluded that the bigger hydrophilic group of DTAC is geometrically favorable for the micelle formation.

In previous paper,[1] we were concerned with the surface adsorption and micelle formation of the mixture of dodecyltrimethylammonium chloride (DTAC) and decylammonium chloride (DeAC), which are different in both the hydrocarbon chain length and the structure of hydrophilic group. Their miscibilities in the adsorbed film and micelle were clarified by applying the thermodynamic equations to the surface tension values measured as a function of the total molality and composition of the surfactant mixture in the aqueous solution. The results indicated that there exists a large difference in miscibility between the adsorbed film and the micelle. This forms a striking contrast to the mixture of surfactants different only in the hydrocarbon chain length[2] and to the mixtures of surfactants different only in the counter ion.[3,4] To make sure how the hydrophilic group influences on the miscibility of the surfactants, we focus our attention to the mixture of surfactants different only in hydrophilic group; DTAC and dodecylammonium chloride (DAC) are chosen as the surfactants. The adsorption and micelle formation of such mixtures have been studied by some workers.[5-8] However, most of them relied on the regular solution theory which is inapplicable to the adsorbed film and micelle of ionic surfactants. In addition, they did not call their attention to the difference in miscibility between the adsorbed film and micelle.

The surface tension of aqueous solution of DTAC–DAC mixture has been measured as a function of total molality and composition at 298.15 K under atmospheric pressure. The results have been analyzed with the aid of our thermodynamic treatment.

Experimental

Dodecyltrimethylammonium chloride and dodecylammonium chloride were synthesized and purified by the methods described previously.[9,10] Their purities were confirmed by observing there are no minimum on the surface tension vs. molality curves. Water used for the preparation of surfactant solution was triply distilled from dilute alkaline permanganate solution.

The surface tension was measured by drop volume method at 298.15 K under atmospheric pressure.[11] The values of surface tension were reproducible with 0.05 mN m^{-1}.

Results and Discussion

The total molality of surfactants m and the composition X_2 are defined as shown in Table 1. Here the m_1 and m_2 are the molalities of dodecyltrimethylammonium chloride (DTAC) and dodecylammonium chloride (DAC), respectively. The γ vs. m curves observed at 298.15 K under atmospheric pressure are shown in Fig. 1. The break point of the curve refers to the critical micelle concentration (cmc). The shape of the curve of mixture changes regularly from that of pure DTAC to that of pure DAC. We also observe that the γ value of micellar solution of surfactant mixture increases with increasing m; its slope is steep compared with that of DAC and decylammonium chloride (DeAC) mixture.[2]

The γ vs. X_2 plot obtained by reading the γ value at a given m from Fig. 1 is shown together with the surface tension at the cmc, γ^C, vs. X_2 plot in Fig. 2. The γ and γ^C values decrease with increasing X_2. In Fig. 3, the value of m required to attain a γ value is plotted against X_2 together with the value of cmc, C. The larger the composition of DAC is, the smaller the total molality of surfactants is. Furthermore, it should be noted that the slope of m vs. X_2 curve is appreciably different from that

Table 1. Definitions of Total Quantity and Composition

	Bulk	Adsorbed film	Micelle
Total quantity	$m=m_1+m_2$	$\Gamma^H=\Gamma^H_{1+}+\Gamma^H_{2+}$	$N^M=N^M_{1+}+N^M_{2+}$
Composition	$X_2=m_2/m$	$X^H_2=\Gamma^H_{2+}/\Gamma^H$	$X^M_2=N^M_{2+}/N^M$

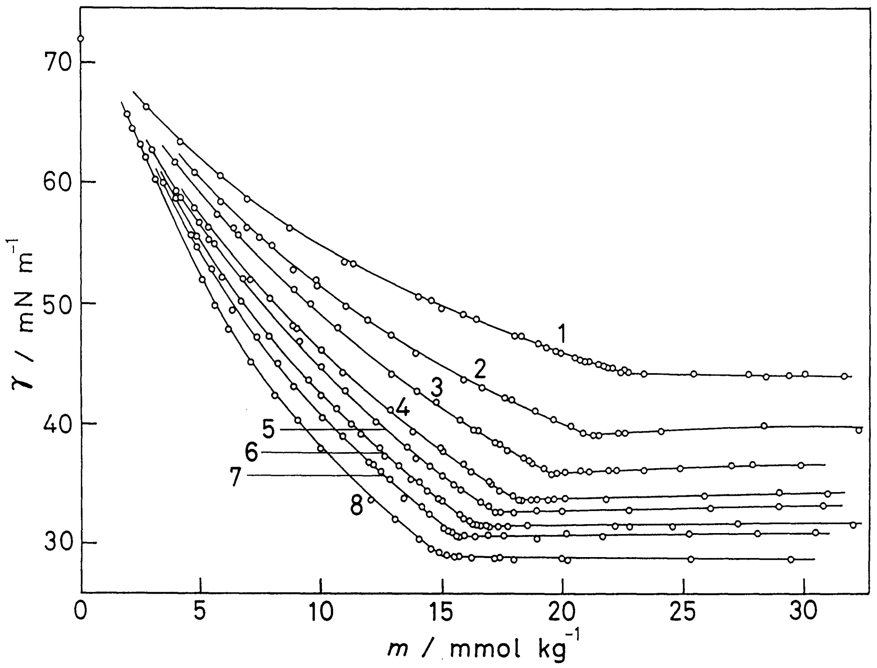

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) X_2=0; (2) 0.125; (3) 0.250; (4) 0.400; (5) 0.500; (6) 0.624; (7) 0.750; (8) 1.

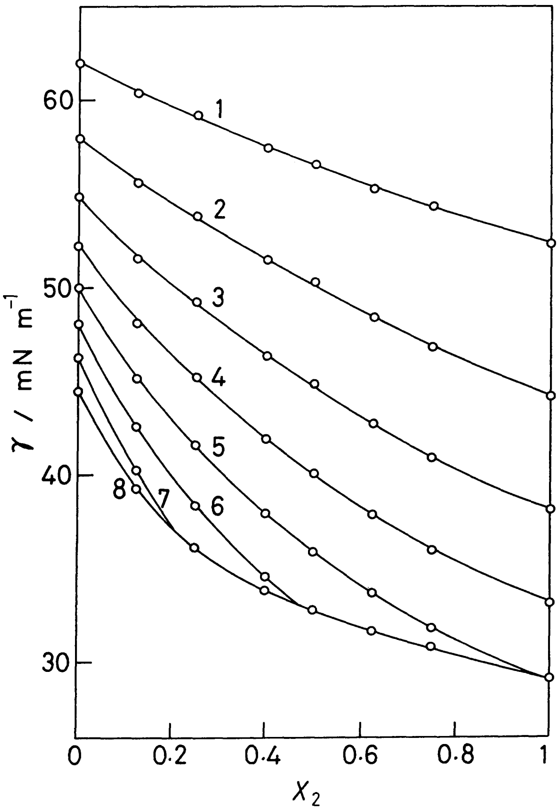

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) m=5 mmol kg^{-1}; (2) 7.5; (3) 10; (4) 12.5; (5) 15; (6) 17.5; (7) 20; (8) γ_c vs. X_2.

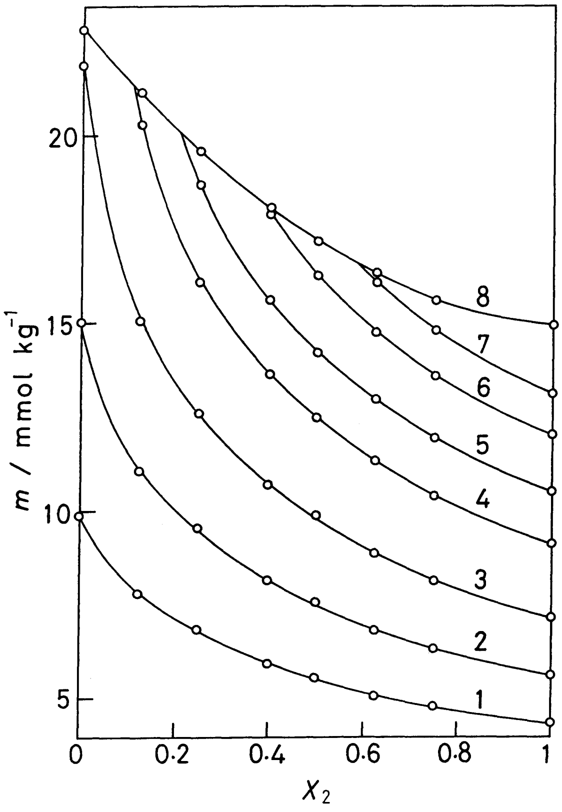

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) γ=55 mN m^{-1}; (2) 50; (3) 45; (4) 40; (5) 37; (6) 34; (7) 32; (8) C vs. X_2.

of C vs. X_2 curve. This behavior is in contrast with that of DAC–DeAC mixture.

Before going into the argument about the miscibility of surfactants, let us define thermodynamic quantities of the adsorbed film and micelle corresponding to m and X_2. In our method, the thermodynamic states of adsorbed film and micelle are described by use of excess quantities. The excess number of moles of component i per unit area (surface density) Γ_i^H in the interfacial region is defined with reference to the two dividing planes introduced so as to make the excess numbers of moles of water and air zero.[12,13] On the other hand, the excess number of component i N_i^M in a micelle particle is defined with reference to the spherical dividing surface chosen so as to make that of water zero.[14] Accordingly, the total surface density of surfactants Γ^H, the composition in the adsorbed film X_2^H, the total number of surfactant in a micelle particle N^M, and the composition in the micelle X_2^M are defined as shown in Table 1. Here the subscripts 1+ and 2+ represent the dodecyltrimethylammonium (DTA) and dodecylammonium (DA) ions, respectively. Because of the electroneutral condition, the surface density of chloride ion and its number in a micelle particle are equal to Γ^H and N^M, respectively.

Now let us examine the adsorption and micelle formation of surfactant mixture. Here we assume its aqueous solution to be ideal, since the concentration is considerably small.

At Concentration below the cmc. When the aqueous solution of DTAC and DAC mixture is free from micelles, the Γ^H value is evaluated by applying

$$\Gamma^H = -(m/2RT)(\partial\gamma/\partial m)_{T,p,X_2} \qquad (1)$$

to the γ vs. m curve in Fig. 1.[13] The values are plotted against the total molality at constant composition in Fig. 4. The Γ^H value increases with increasing molality and decreases with increasing the composition of DTAC. The large size of the hydrophilic group of DTA ion is said to reduce the adsorption of surfactants.

Next let us evaluate the composition of adsorbed film; X_2^H is related thermodynamically to the X_2 as follows:[13]

$$X_2^H = X_2 - (X_1X_2/RT\Gamma^H)(\partial\gamma/\partial X_2)_{T,p,m}. \qquad (2)$$

By applying Eq. 2 to the γ vs. X_2 curve depicted in Fig. 2 and introducing the Γ^H value given in Fig. 4, the X_2^H value is evaluated and shown in the form of γ vs. X_2^H curve together with the γ vs. X_2 curve in Fig. 5. The diagram indicates that the adsorbed film is richer in surface active DAC than the bulk solution. Furthermore, it is a cigar shape. Alternatively the composition of adsorbed film is also evaluated by applying

$$X_2^H = X_2 - 2(X_1X_2/m)(\partial\gamma/\partial m)_{T,p,\gamma} \qquad (3)$$

to the m vs. X_2 curve depicted in Fig. 3. The results are

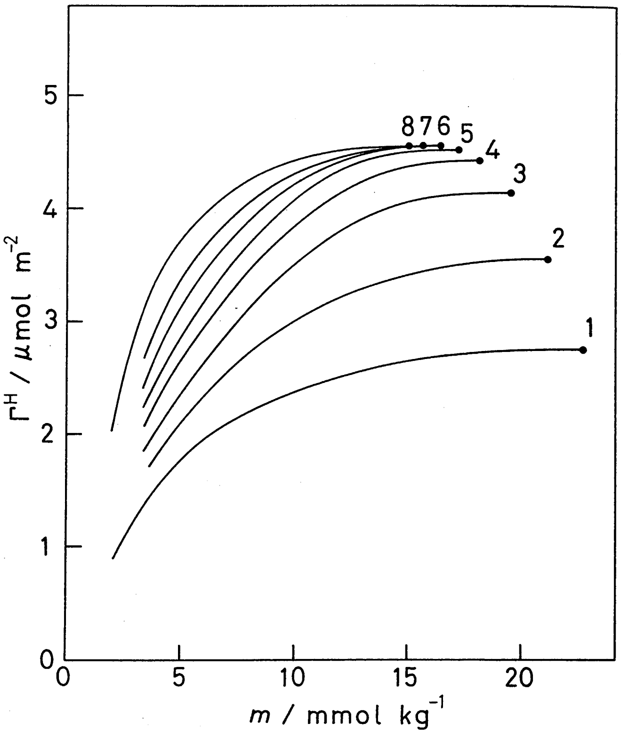

Fig. 4. Total surface density vs. total molality curves at constant composition: (1) X_2=0; (2) 0.125; (3) 0.250; (4) 0.400; (5) 0.500; (6) 0.624; (7) 0.750; (8) 1.

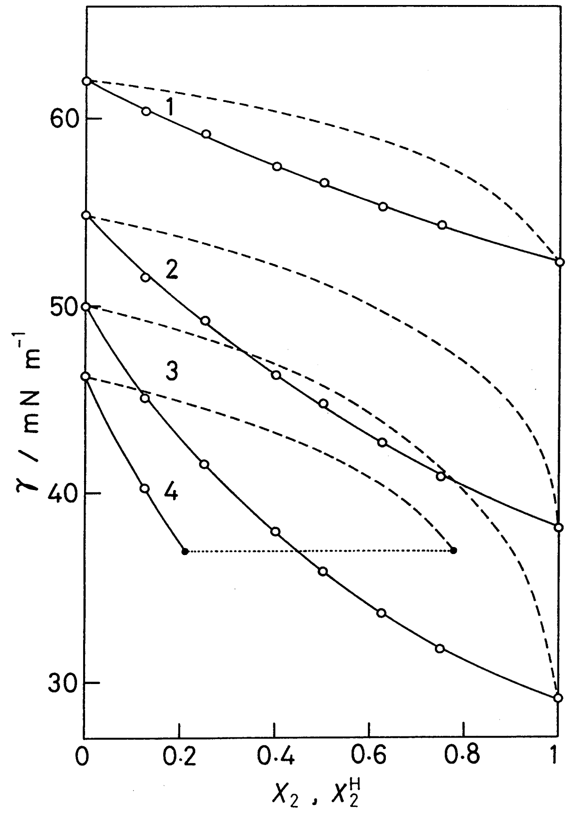

Fig. 5. Surface tension vs. composition curves at constant total molality: (1) m=5 mmol kg^{-1}; (2) 10; (3) 15; (4) 20; (●) γ^C; (—) X_2; (---) X_2^H.

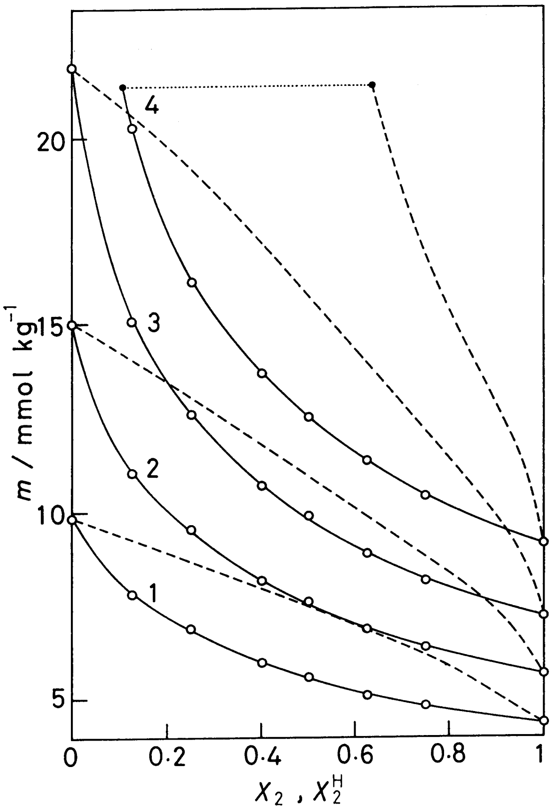

Fig. 6. Total molality vs. composition curves at constant surface tension: (1) γ=55 mN m^{-1}; (2) 50; (3) 45; (4) 40; (●) C; (—) X_2; (---) X_2^H.

displayed by the m vs. composition diagram in Fig. 6. The diagram at constant surface tension has a different shape from the diagram of Fig. 5; the m vs. X_2^H curve has a region convex downward at low surface tension. Taking into account that the m vs. X_2^H curve is convex upward in the whole range of composition in the case of the DAC–DeAC mixture which is considered to behave ideally in the adsorbed film,[2)] we may say that the mixing of DTAC and DAC molecules in the adsorbed film is slightly nonideal. This result is in harmony with that of the nonionic mixture of octanol–2-(octylsulfinyl)ethanol (OSE) whose hydrophilic groups are different.[15)] Therefore, the difference in the chemical structure of hydrophilic group is said to make a large influence on the interaction between the surfactants and accordingly their miscibility in the adsorbed film.

At the Critical Micelle Concentration. Let us now examine the composition of mixed micelle at the cmc. The X_2^M value is estimated from the dependence of C on X_2 by using[14)]

$$X_2^M = X_2 - 2(X_1X_2/C)(\partial C/\partial X_2)_{T,p}. \quad (4)$$

The result is shown in the form of the C vs. X_2^M curve together with the C vs. X_2 curve in Fig. 7; the micelle is richer in DAC as the adsorbed film is. Furthermore, the

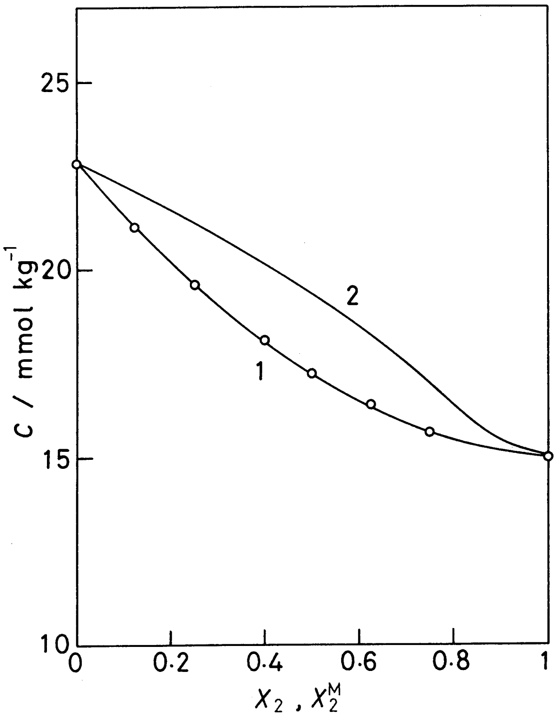

Fig. 7. Critical micelle concentration vs. composition curves: (1) C vs. X_2; (2) C vs. X_2^M.

C vs. X_2^M curve is convex downward near X_2=1 and the diagram of micelle formation has a deformed cigar shape. This shape is fairly different from a swollen cigar shape of the diagrams of DAC–DeAC and decylammonium bromide (DeAB)–DeAC mixtures (Fig. 9 in Ref. 3). It may be said, therefore, that the DTAC and DAC mixture shows a negative deviation from the ideality in the micelle particle abundant in DAC. Further, there seems to be a difference in shape between the diagrams of adsorption (Fig. 6) and micelle formation (Fig. 7). We suppose that the miscibility of DTAC and DAC in the micelle is different from that in the adsorbed film. This will be discussed later.

The phase diagram of micelle formation provides a qualitative information about the change in monomer concentration with m in a concentration range above the cmc. The corresponding information about the change in surface tension is obtained from the γ^C vs. composition diagram drawn by making use of Figs. 2 and 7; the diagram is shown in Fig. 8. The diagram indicates that the surface tension of micellar solution increases with increasing m. This is consistent with the experimental results shown in Fig. 1. Further, the fact that the increase in γ of the DTAC–DAC system is more significant than that of the DAC–DeAC system can be explained by a large difference between the γ^C values of DTAC and DAC.

Finally let us concern with the difference in composition between the adsorbed film and micelle. The composition $X_2^{H,C}$ of the adsorbed film in equilibrium with the micelle at the cmc is evaluated by applying

$$X_2^{\mathrm{H,C}} = X_2^{\mathrm{M}} - (X_1X_2/RT\Gamma^{\mathrm{H,C}})(\partial\gamma^{\mathrm{C}}/\partial X_2)_{T,p} \qquad (5)$$

to the γ^{C} vs. X_2 curve given in Fig. 8.[2,13] Here, the $\Gamma^{\mathrm{H,C}}$ is the total surface density of mixture at the cmc which is estimated from Fig. 4. The $X_2^{\mathrm{H,C}}$ value evaluated is drawn in the form of the γ^{C} vs. $X_2^{\mathrm{H,C}}$ curve (dashed line) in Fig. 9 together with the γ^{C} vs. X_2^{M} curve. The value

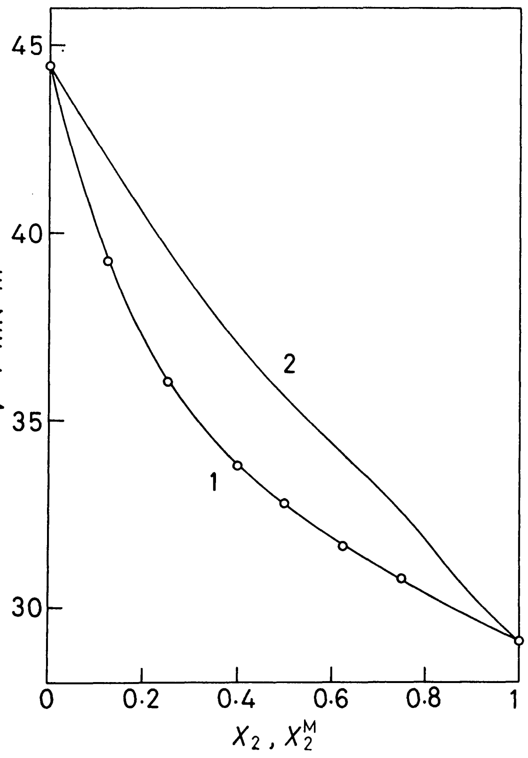

Fig. 8. Surface tension at the critical micelle concentration vs. composition curves: (1) γ_{C} vs. X_2; (2) γ_{C} vs. X_2^{M}.

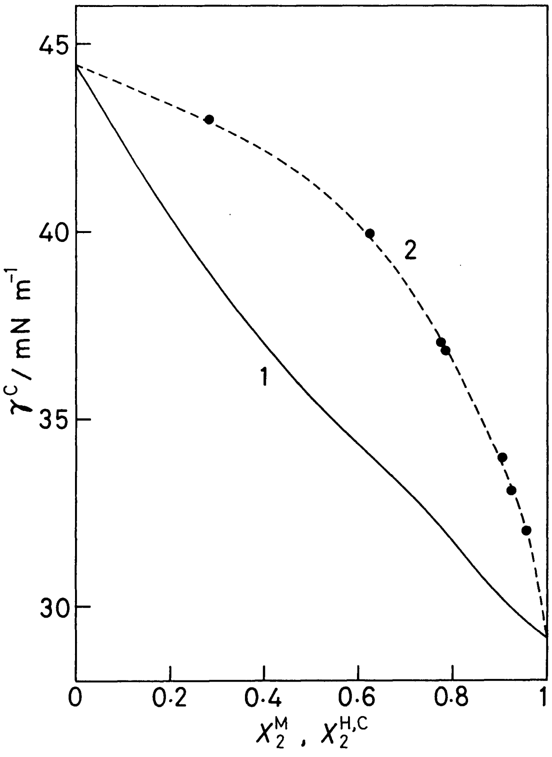

Fig. 9. Surface tension at the critical micelle concentration vs. composition curves: (1) γ_{C} vs. X_2^{M} curve; (2) γ_{C} vs. $X_2^{\mathrm{H,C}}$ curve; (●) the $X_2^{\mathrm{H,C}}$ value obtained by extrapolation.

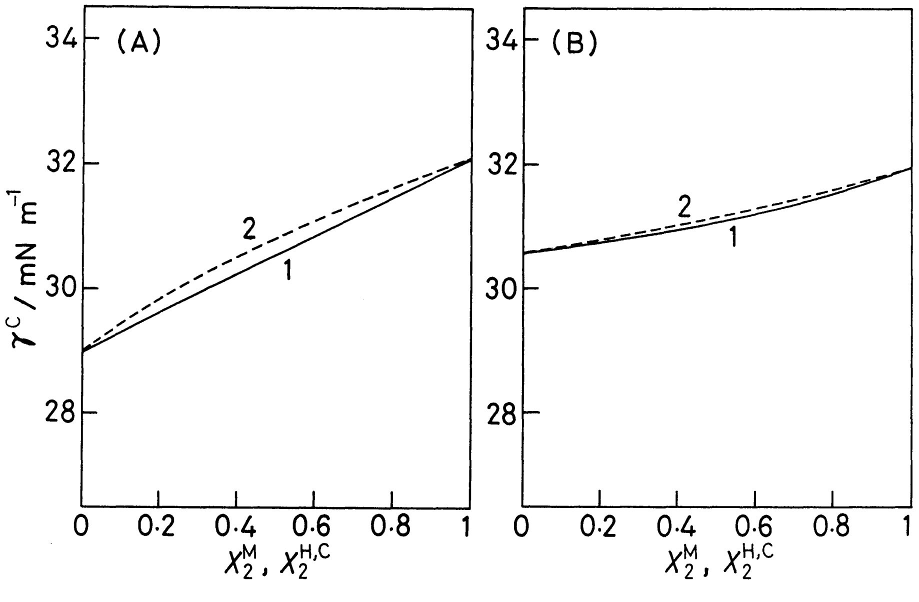

Fig. 10. Surface tension at the critical micelle concentration vs. composition of DeAC curves: (A) DAC–DeAC system; (B) DeAB–DeAC system; (1) γ_{C} vs. X_2^{M}; (2) γ_{C} vs. $X_2^{\mathrm{H,C}}$.

of $X_2^{H,C}$ is also obtained by extrapolating the m vs. X_2^H (or γ vs. X_2^H) curve to the cmc (or γ^C) and is shown by closed circle in Fig. 9. Its agreement with the dashed line within an experimental error supports the view that the thermodynamic treatment used here is reasonable. From Fig. 9, the composition of DAC in the micelle is found to be remarkably smaller than that in the adsorbed film. This behavior forms a striking contrast to that of the DAC–DeAC and DeAB–DeAC mixtures (Fig. 10).[2,3] We may say that the size of hydrophilic group of surfactant brings about the difference in the miscibility of surfactants between the micelle and the adsorbed film. Furthermore, it is worthwhile to note that the micelle is abundant in the surfactant having a bigger hydrophilic group. The similar results have been obtained for the DTAC–DeAC and octanol–OSE systems.[1,15] We conclude that the bigger hydrophilic group of DTA ion is geometrically favorable for the spherical micelle formation.

Further information about the influence of the size and chemical structure of hydrophilic group of surfactant on the miscibility will be obtained by examining the mixtures of DAC with the dodecylmethylammonium chloride and dodecyldimethylammonium chloride.

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