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Miscibility of 2-(Octylsulfinyl)ethanol and Decylammonium Chloride in the Adsorbed Film and Micelle

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The surface tension of the aqueous solution of 2-(octylsulfinyl)ethanol (OSE) and decylammonium chloride (DeAC) mixture was measured as a function of total molality and composition of surfactants at 298.15 K under atmospheric pressure. The total surface density and compositions in the adsorbed film and micelle of the mixture were evaluated by applying thermodynamic relations to experimental results. It was found that the phase diagrams obtained for the adsorption and micelle formation of the mixture are different in shape from those of 2-(decylsulfinyl)ethanol (DeSE)–OSE and dodecylammonium chloride (DAC)–DeAC mixtures which are assumed to mix ideally in the adsorbed film and micelle. Such a nonideal behavior was attributed to the attractive interaction between OSE and DeAC molecules. Further, the interaction is concluded to be more attractive in the micelle than in the adsorbed film.

In previous papers, the surface adsorption and micelle formation of nonionic–nonionic[1–3] and cationic–cationic[4–7] surfactant mixtures have been investigated by applying the thermodynamic relations derived on the basis of excess thermodynamic quantities to measured surface tension. It has been demonstrated that the relation among the compositions of surfactants in the bulk phase, adsorbed film, and micelle provides important information about their miscibility.

There were many reports that nonionic and ionic surfactants mix nonideally in adsorbed films and micelles.[8–17] However most of them relied on the analysis using the regular solution approximation which is considered not to be appropriate to describe the mixed adsorbed films and micelles.[4,7,15,16,18]

Now it is necessary to apply our thermodynamic treatment to nonionic–ionic mixed surfactant systems. In the present study, we choose the mixture of 2-(octylsulfinyl)ethanol (OSE) and decylammonium chloride (DeAC), because we have already investigated (i) the mixed adsorbed film of OSE and DeAC[19] in a dilute concentration range and (ii) the surface adsorption and micelle formation of mixed surfactant systems which contain either OSE or DeAC as one constituent.[1–6]

Experimental

2-(Octylsulfinyl)ethanol and decylammonium chloride were synthesized and purified by the methods described previously.[2,20,21] Water was triply distilled from dilute alkaline permanganate solution.

The equilibrium surface tension was measured by the drop volume technique at 298.15 K under atmospheric pressure.[22] Surface tension values were reproducible within 0.05 mN m^{-1}.

Results and Discussion

In order to investigate the miscibility of nonionic and ionic surfactants in the adsorbed film and micelle, it is appropriate to employ the total molality $\hat{m}$ of surfactants and the mole fraction $\hat{X}_2$ of surfactant 2 in the total surfactant introduced previously[7,18] as the experimental variables. In the case of the present system, $\hat{m}$ and $\hat{X}_2$ are related to the molality m_i of surfactant i as follows:

$$\hat{m} = m_1 + 2m_2 \tag{1}$$

and

$$\hat{X}_2 = 2m_2/\hat{m}, \tag{2}$$

where the subscripts 1 and 2 express OSE and DeAC, respectively.

The surface tension γ was measured as a function of $\hat{m}$ and $\hat{X}_2$ at 298.15 K under atmospheric pressure. The γ vs. $\hat{m}$ curve obtained at constant $\hat{X}_2$ is shown in Fig. 1. It is found that the curve has a distinct break point where the micelle formation begins. The concentration of this point is referred to as the critical micelle concentration (cmc). Another break point is seen on the curve at a relatively low concentration; this point was proved to result from the phase transformation between the gaseous and expanded states of adsorbed film.[19] The γ vs. $\hat{X}_2$ curves at constant $\hat{m}$ depicted by replotting Fig. 1 are shown together with the surface tension at the cmc

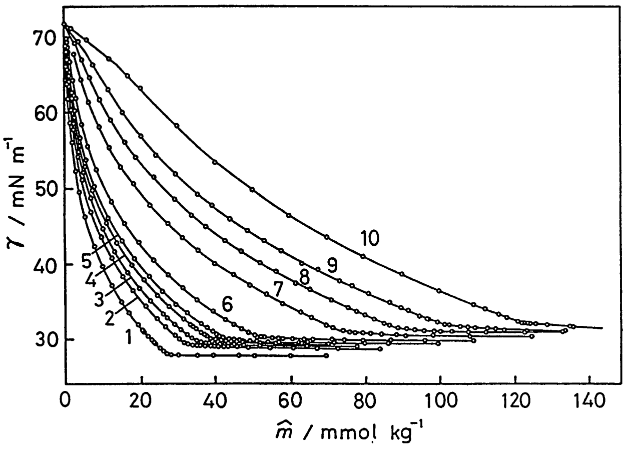

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) $\hat{X}_2$=0; (2) 0.349; (3) 0.443; (4) 0.550; (5) 0.613; (6) 0.725; (7) 0.889; (8) 0.941; (9) 0.972; (10) 1.

γ^C vs. $\hat{X}_2$ curve in Fig 2. Both the γ and γ^C values increase as the composition of DeAC increases. But the curves are quite different in shape from each other; the γ^C vs. $\hat{X}_2$ curve is concave downward at a small composition and concave upward at a large composition, while the γ vs. $\hat{X}_2$ curve is concave upward over the whole range of composition. In Fig. 3, the $\hat{m}$ at constant γ and the cmc $\hat{C}$ are plotted against $\hat{X}_2$. The $\hat{m}$ and $\hat{C}$ values increase with increasing $\hat{X}_2$ and the dependence of $\hat{C}$ on $\hat{X}_2$ resembles that of $\hat{m}$.

Now let us derive the thermodynamic formulae to apply to the nonionic–uni-univalent ionic surfactant system. Adopting the two dividing planes defined so as to make the surface excess numbers of moles of water and air zero simultaneously and assuming an ideal solution, the total differential of surface tension at constant temperature and pressure is written in the form[7]

$$d\gamma = -(RT\hat{\Gamma}^H/\hat{m})d\hat{m} + (RT\hat{\Gamma}^H/\hat{X}_1\hat{X}_2)(\hat{X}_2 - \hat{X}_2^H)d\hat{X}_2, \quad (3)$$

where $\hat{\Gamma}^H$ and $\hat{X}_2^H$ are the total surface density and composition of DeAC in the adsorbed film defined by

$$\hat{\Gamma}^H = \Gamma_1^H + \Gamma_{2+}^H + \Gamma_{2-}^H \quad (4)$$

and

$$\hat{X}_2^H = (\Gamma_{2+}^H + \Gamma_{2-}^H)/\hat{\Gamma}^H, \quad (5)$$

respectively. Here Γ_1^H, Γ_{2+}^H, and Γ_{2-}^H are the surface excess numbers of moles of OSE, decylammonium ion, and chloride ion, respectively. Since the condition of electroneutrality holds, Γ_{2+}^H is equal to Γ_{2-}^H.

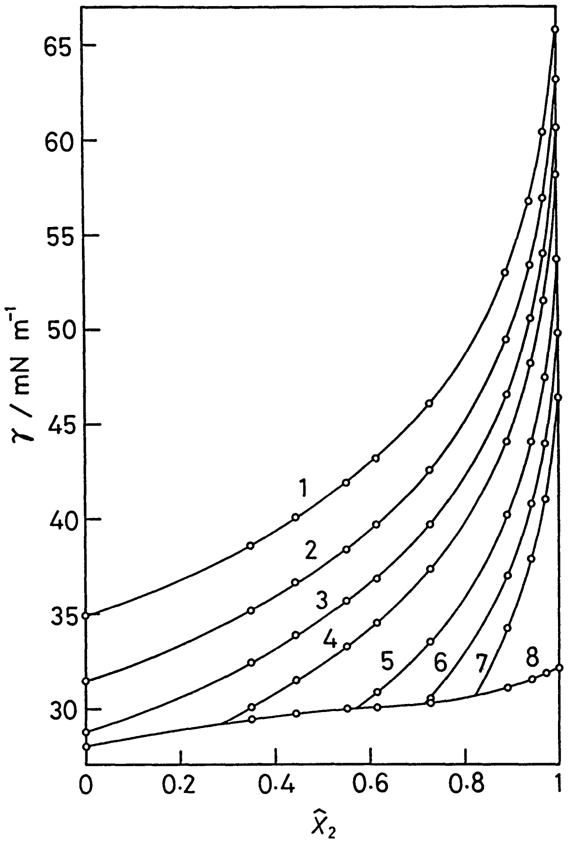

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) $\hat{m}$=15 mmol kg^{-1}; (2) 20; (3) 25; (4) 30; (5) 40; (6) 50; (7) 60; (8) γ^C vs. $\hat{X}_2$.

Miscibility in the Adsorbed Film at a Concentration below the cmc. First, let us examine the state of

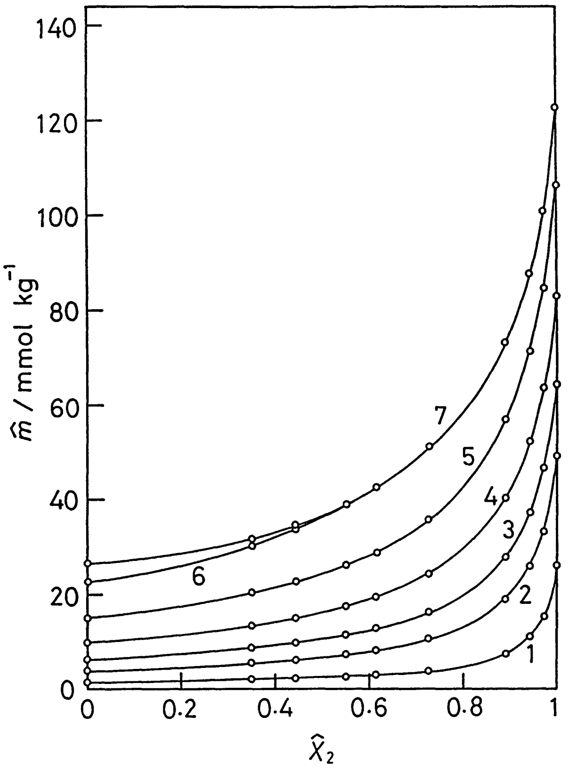

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) γ=60 mN m^{-1}; (2) 50; (3) 45; (4) 40; (5) 35; (6) 30; (7) $\hat{C}$ vs. $\hat{X}_2$.

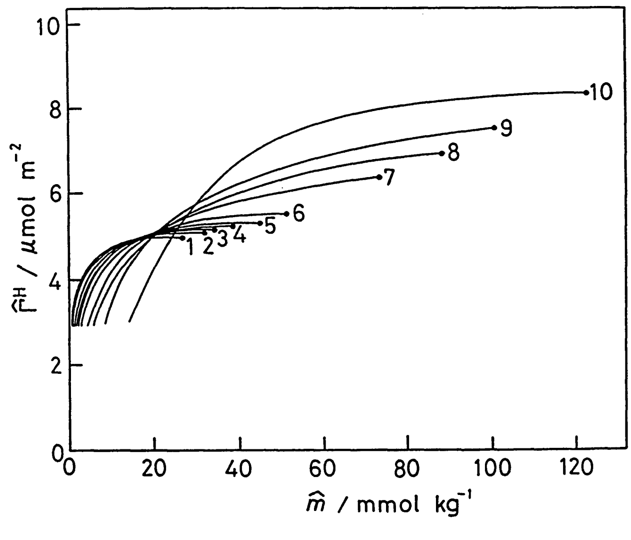

Fig. 4. Total surface density vs. total molality curves at constant composition: (1) $\hat{X}_2$=0; (2) 0.349; (3) 0.443; (4) 0.550; (5) 0.613; (6) 0.725; (7) 0.889; (8) 0.941; (9) 0.972; (10) 1; (●) total surface density at the cmc $\hat{\Gamma}^{H,C}$.

adsorbed film in terms of the total surface density $\hat{\Gamma}^H$. The value of $\hat{\Gamma}^H$ is calculated by applying the equation

$$\hat{\Gamma}^H = -(\hat{m}/RT)(\partial\gamma/\partial\hat{m})_{T,p,\hat{X}_2} \tag{6}$$

to the γ vs. $\hat{m}$ curve illustrated in Fig. 1; the value is plotted against $\hat{m}$ at constant $\hat{X}_2$ in Fig. 4. It is seen that the $\hat{\Gamma}^H$ value increases with increasing $\hat{m}$ and approaches to a saturated value at a concentration near the cmc. It is also seen that the $\hat{\Gamma}^H$ vs. $\hat{m}$ curve changes its shape from that of OSE to that of DeAC.

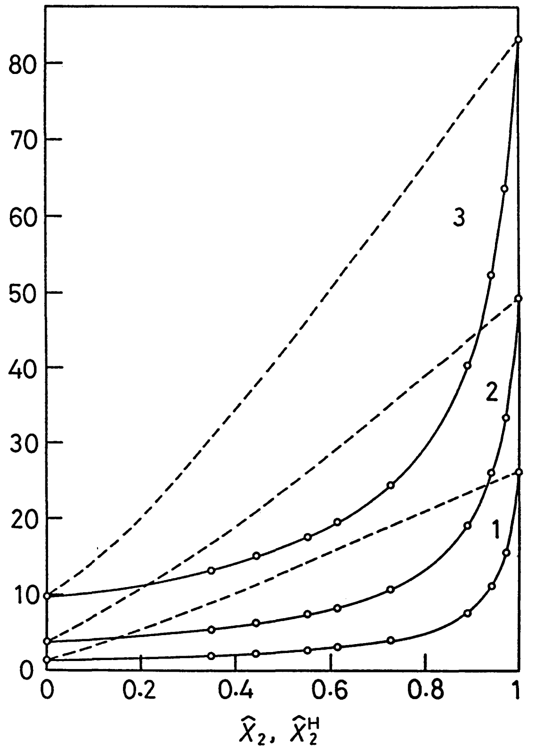

Fig. 5. Total molality vs. composition curves at constant surface tension: (1) γ=60 mN m^{-1}; (2) 50; (3) 40; (——) $\hat{X}_2$; (-----) $\hat{X}_2^H$.

In order to clarify the miscibility of OSE and DeAC in the adsorbed film, it is useful to examine the composition in the adsorbed film. The value of $\hat{X}_2^H$ at a given γ is estimated by applying the following equation derived from Eq. 3 to the $\hat{m}$ vs. $\hat{X}_2$ curve shown in Fig. 3:

$$\hat{X}_2^H = \hat{X}_2 - (\hat{X}_1\hat{X}_2/\hat{m})(\partial\hat{m}/\partial\hat{X}_2)_{T,p,\gamma}. \tag{7}$$

The evaluated values are presented in the form of $\hat{m}$ vs. $\hat{X}_2^H$ curves at γ=60, 50, and 40 mN m^{-1} together with the corresponding $\hat{m}$ vs. $\hat{X}_2$ curves in Fig. 5. This diagram tells us that OSE and DeAC molecules are miscible with each other over the whole composition range at water/air interface and that the adsorbed film is richer in more surface active OSE molecules. Furthermore, the diagram may be said to take the shape of a distorted cigar when compared with those of 2-(decylsulfinyl)ethanol (DeSE)–OSE and dodecylammonium chloride (DAC)–DeAC systems[2,4] drawn in Fig. 6. Taking into account that the $\hat{m}$ vs. $\hat{X}_2^H$ curve deviates negatively from the straight line connecting the $\hat{m}$ values of pure OSE and DeAC, we may conclude that the OSE and DeAC molecules mix nonideally with each other in the adsorbed film.

Miscibility in the Micelle and Adsorbed Film at the cmc. Next let us proceed to see how OSE and DeAC molecules mix in the micellar state. The composition of surfactant in the micelle is defined by

$$\hat{X}_2^M = (N_{2+}^M + N_{2-}^M)/(N_1^M + N_{2+}^M + N_{2-}^M), \tag{8}$$

where N_i^M is the excess number of moles of i-species per micelle particle with reference to the dividing surface which makes the excess number of moles of water zero. Since the total molality of monomeric surfactant is

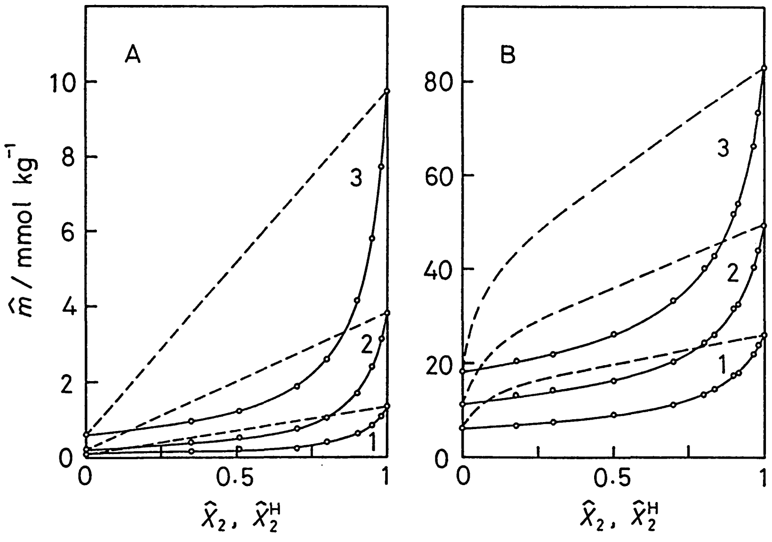

Fig. 6. Total molality vs. composition curves at constant surface tension: (A) DeSE–OSE system; (B) DAC–DeAC system; (1) γ=60 mN m^{-1}; (2) 50; (3) 40; (——) $\hat{X}_2$; (-----) $\hat{X}_2^H$.

assumed to be equal to $\hat{C}$ in a limited concentration range near the cmc, the following relation holds at constant T and p:7,18)

$$(RT/\hat{C})\mathrm{d}\hat{C} = (RT/\hat{X}_1\hat{X}_2)(\hat{X}_2 - \hat{X}_2^{\mathrm{M}})\mathrm{d}\hat{X}_2. \tag{9}$$

Then the value of $\hat{X}_2^{\mathrm{M}}$ is immediately evaluated from the dependence of $\hat{C}$ on $\hat{X}_2$:

$$\hat{X}_2^{\mathrm{M}} = \hat{X}_2 - (\hat{X}_1\hat{X}_2/\hat{C})(\partial\hat{C}/\partial\hat{X}_2)_{T,p}. \tag{10}$$

Figure 7 shows the plot of $\hat{C}$ against $\hat{X}_2^{\mathrm{M}}$ together with that of $\hat{C}$ vs. $\hat{X}_2$ curve of OSE–DeAC system deviates negatively from the straight line joining the $\hat{C}$ values of pure OSE and DeAC, although those of DeSE–OSE and DAC–DeAC systems given in Fig. 8 deviate positively. This finding indicates that OSE and DeAC molecules mix nonideally in the micelle as well as in the adsorbed film. These nonideal behavior is attributable to the attractive interaction between OSE and DeAC molecules.

On the other hand, the γ^{C} value is plotted against $\hat{X}_2$ and $\hat{X}_2^{\mathrm{M}}$ in Fig. 9. This diagram conveys some information concerning the γ vs. $\hat{m}$ curve above the cmc:2–5) the curve of mixture is expected to increase slightly at a concentration range above the cmc. Taking into consideration that the γ values of pure OSE and DeAC decrease slightly at a concentration above the cmc, the above expectation does not contradict the results shown in Fig. 1.

Now, it is useful to inquire the relation between the compositions of micelle and adsorbed film at the cmc. Since $\hat{m}$ is assumed to be equal to $\hat{C}$ at the cmc, Eq. 3 is rewritten as

$$\mathrm{d}\gamma^{\mathrm{C}} = -(RT\hat{\Gamma}^{\mathrm{H,C}}/\hat{C})\mathrm{d}\hat{C} + (RT\hat{\Gamma}^{\mathrm{H,C}}/\hat{X}_1\hat{X}_2)(\hat{X}_2 - \hat{X}_2^{\mathrm{H,C}})\mathrm{d}\hat{X}_2, \tag{11}$$

where $\hat{\Gamma}^{\mathrm{H,C}}$ and $\hat{X}_2^{\mathrm{H,C}}$ are the total surface density and composition of adsorbed film at the cmc, respectively. Combination of Eqs. 9 and 11 leads to the equation

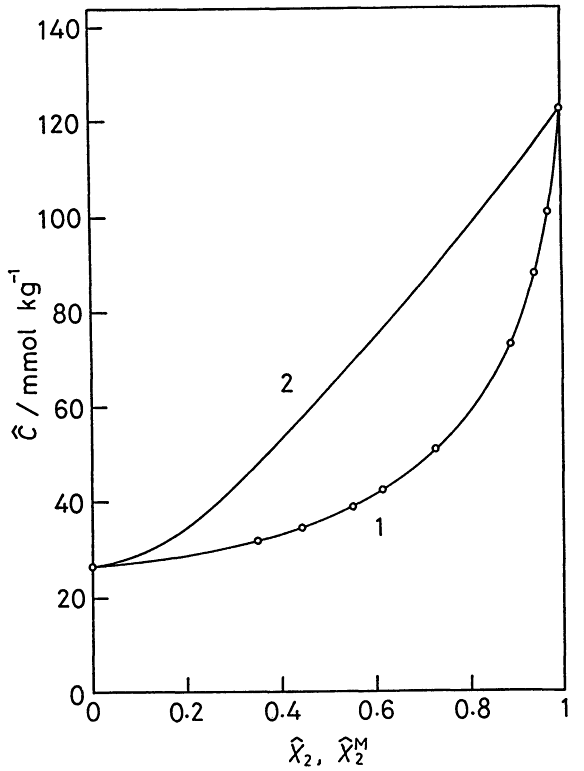

Fig. 7. Critical micelle concentration vs. composition curves: (1) $\hat{C}$ vs. $\hat{X}_2$; (2) $\hat{C}$ vs. $\hat{X}_2^{\mathrm{M}}$.

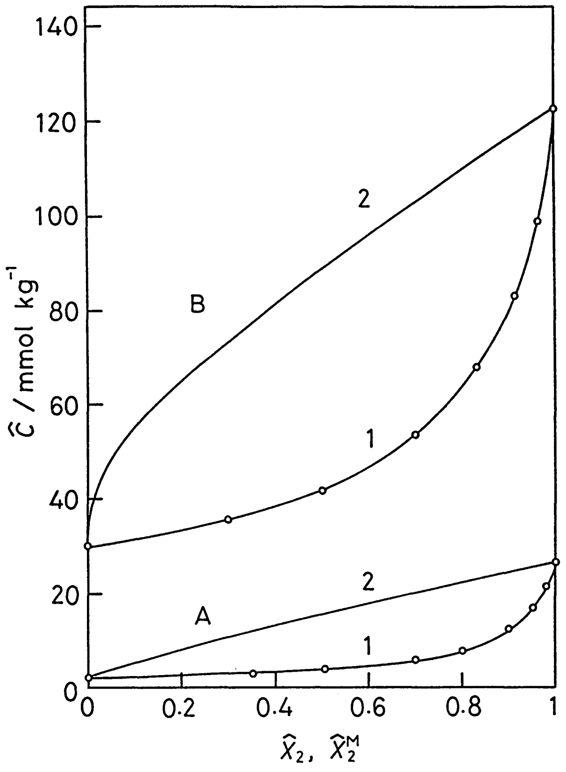

Fig. 8. Critical micelle concentration vs. composition curves: (A) DeSE–OSE system; (B) DAC–DeAC system; (1) $\hat{C}$ vs. $\hat{X}_2$; (2) $\hat{C}$ vs. $\hat{X}_2^{\mathrm{M}}$.

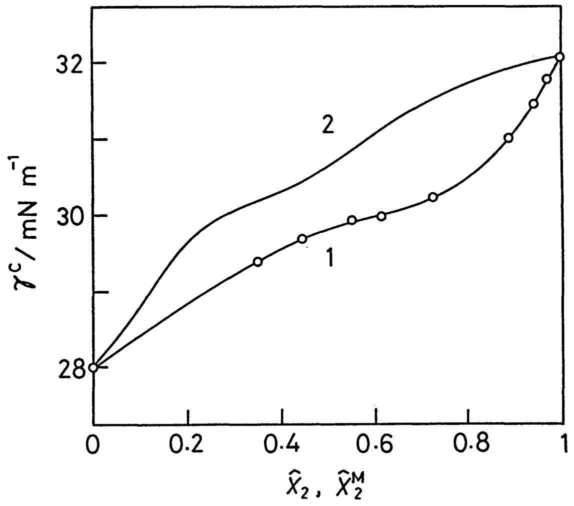

Fig. 9. Surface tension at the cmc vs. composition curves: (1) γ^{C} vs. $\hat{X}_2$; (2) γ^{C} vs. $\hat{X}_2^{\mathrm{M}}$.

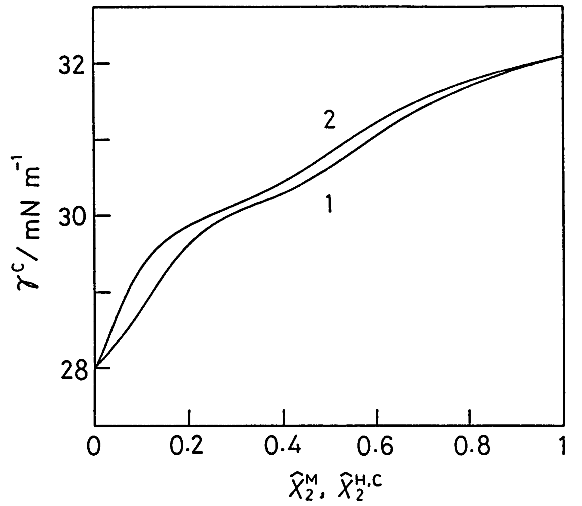

Fig. 10. Surface tension at the cmc vs. composition curves: (1) γ^C vs. $\hat{X}_2^M$; (2) γ^C vs. $\hat{X}_2^{H,C}$.

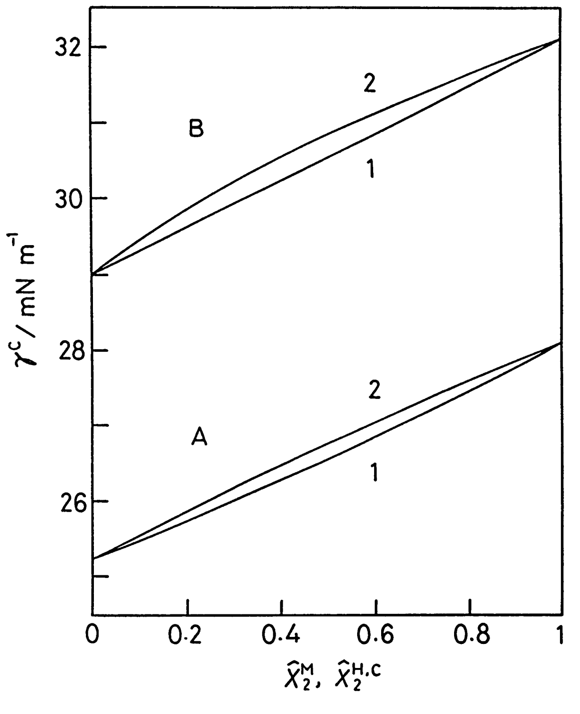

Fig. 11. Surface tension at the cmc vs. composition curves: (A) DeSE–OSE system; (B) DAC–DeAC system; (1) γ^C vs. $\hat{X}_2^M$; (2) γ^C vs. $\hat{X}_2^{H,C}$.

$$\hat{X}_2^{H,C}=\hat{X}_2^M-(\hat{X}_1\hat{X}_2/RT\hat{\Gamma}^{H,C})(\partial\gamma^C/\partial\hat{X}_2)_{T,p}. \qquad (12)$$

Applying Eq. 12 to the γ^C vs. $\hat{X}_2$ curve illustrated in Fig. 2 and making use of the $\hat{\Gamma}^{H,C}$ value estimated by the extrapolation of $\hat{\Gamma}^H$ vs. $\hat{m}$ curve to the cmc in Fig. 4, we can evaluate the value of $\hat{X}_2^{H,C}$. The results are shown in Fig. 10. It is seen that the diagram has a deformed shape compared with those of the DeSE–OSE and DAC–DeAC systems given in Fig. 11. This is closely associated with the nonideal mixing of OSE and DeAC molecules in the adsorbed film and micelle. Furthermore, the γ^C vs. $\hat{X}_2^{H,C}$ curve is found to deviate more positively than the γ^C vs. $\hat{X}_2^M$ curve. Therefore, we may conclude that the interaction between OSE and DeAC molecules are more attractive in the micelle than in the adsorbed film.

It is probable from the thermodynamic viewpoint that nonionic and cationic surfactants form a negative azeotrope in the adsorbed film and micelle if their γ vs. $\hat{m}$ curves are close to each other over the whole concentration range. This will be realized for the mixture of OSE and DAC.[23]

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