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Interaction of Sodium 4′-(Butylamino)azobenzene-4-sulfonate with 2-(Octylsulfinyl)ethanol in Adsorbed Film and Micelle

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The surface tension of the aqueous solution of anionic dye and nonionic surfactant mixture was measured as a function of total concentration at various compositions and at 298.15 K under atmospheric pressure. The dye used is sodium 4′-(butylamino)azobenzene-4-sulfonate (SBAS) and the nonionic surfactant is 2-(octylsulfinyl)ethanol (OSE). By use of thermodynamic relations developed previously, the phase diagrams of adsorption and micelle formation were constructed. It was found that SBAS and OSE are completely miscible with each other in the adsorbed film and that the adsorbed film is enriched in OSE compared with the solution except for a composition close to pure OSE. It was concluded that SBAS and OSE interact attractively with each other in the adsorbed and micellar states and, furthermore, that the interaction is more attractive in the micelle than in the adsorbed film. The miscibility of dye and nonionic surfactant is suggested to play an important role in the working of nonionic surfactant as a levelling agent in dyeing process.

Nonionic surfactants have been used as levelling agents to prevent fibers from unlevelling dyeing. Some investigations have been undertaken to clarify the mechanism of levelling by spectroscopic technique[1,2] and surface tension measurement;[3,4] it is qualitatively said that the adsorption ability of dyes is weakened by forming complex between dye and nonionic surfactant molecules. However the dyeing is not practically carried out in such a surfactant rich region where the complex formation takes place in the solution. So there may exist another mechanism to dye fibers evenly. For a right understanding of dyeing process, it is essential to investigate the adsorption of a mixture of surfactant and dye quantitatively. In this respect it is advantageous to adopt the surface tension measurement of the aqueous solution of the mixture and to analyze experimental results thermodynamically.[5] We use 2-(octylsulfinyl)ethanol (OSE) as a nonionic surfactant and sodium 4′-(butylamino)azobenzene-4-sulfonate (SBAS) as a dye. The surface tension is measured as a function of total concentration of OSE and SBAS at various compositions of the mixture at 298.15 K under atmospheric pressure. The interaction between OSE and SBAS in the mixed adsorbed film and mixed micelle are clarified by using the phase diagrams of adsorption and micelle formation and by comparing the results with those of the OSE and cationic surfactant mixtures.[6,7]

Experimental

2-(octylsulfinyl)ethanol was synthesized and purified by the methods described previously.[8] Sodium 4′-(butylamino)azobenzene-4-sulfonate was synthesized by the method reported in the literature (Chart 1).[9] The purities of OSE and SBAS were checked by elemental analysis. No minimum was detected on the surface tension vs. concentration curve around the critical micelle concentration (cmc) of OSE.

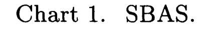

Chart 1. SBAS.

Water distilled triply from alkaline permanganate solution was used. The surface tension was measured by the drop volume method within an error of ±0.05 mN m^{-1} at 298.15 K under atmospheric pressure.[10]

Results and Discussion

To investigate the interaction between anionic dye and nonionic surfactant in the adsorbed film and micelle, the total molality of the solutes $\hat{m}$ and the mole fraction $\hat{X}_2$ of OSE were employed as the experimental variables at constant temperature and pressure; they are defined respectively by

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

and

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

where m_1 and m_2 are the molalities of SBAS and OSE, respectively. Here, the dissociation of component 1 is to be taken into consideration.[6,7,11] The surface tension of the aqueous solution of mixture was measured as a function of $\hat{m}$ at constant $\hat{X}_2$ and plotted against $\hat{m}$ in Fig. 1. It is seen that the γ value decreases with increasing $\hat{m}$ although its $\hat{X}_2$ dependence is considerably complicated. Further the critical micelle concentration $\hat{C}$ seems to be definitely determined at high $\hat{X}_2$ value, while at low $\hat{X}_2$, though the surface tension is almost constant in a high concentration range, it is hard to decide the $\hat{C}$ value. This implies that SBAS does not form the micelle by itself and its micellization is enhanced by the addition of a small amount of OSE.

The variation of γ with $\hat{X}_2$ is shown more clearly by reading the γ value at a given $\hat{m}$ in Fig. 1 and drawing the γ vs. $\hat{X}_2$ plot as shown in Fig. 2, where the surface tension γ^{C} at the cmc is also plotted against $\hat{X}_2$. The γ vs. $\hat{X}_2$ curve varies monotonously at a low

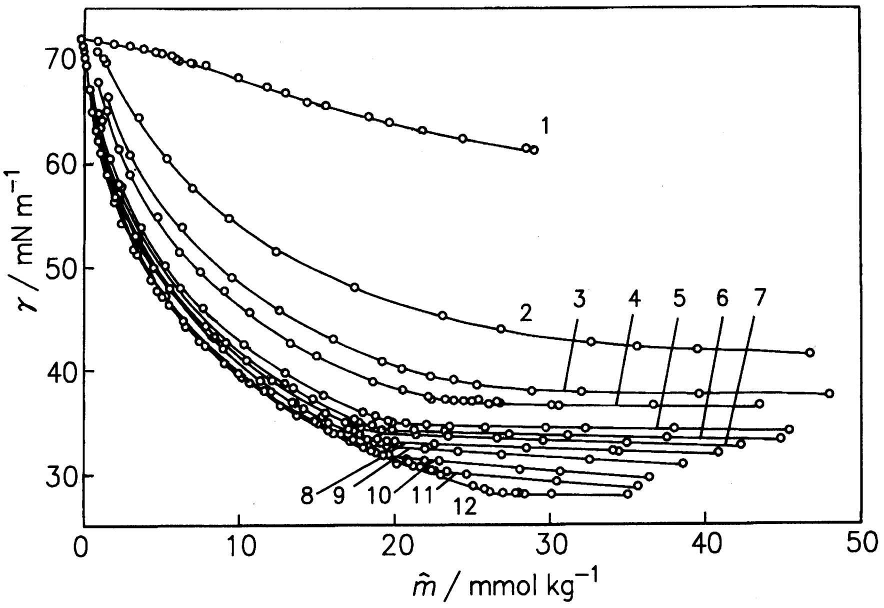

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) $\hat{X}_2=0$; (2) 0.111; (3) 0.250; (4) 0.333; (5) 0.538; (6) 0.600; (7) 0.667; (8) 0.740; (9) 0.818; (10) 0.905; (11) 0.960; (12) 1.

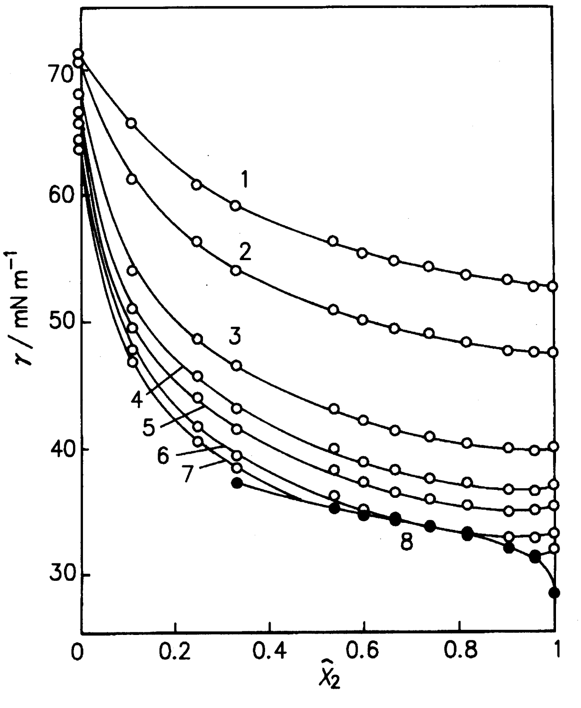

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) $\hat{m}=3$ mmol kg^{-1}; (2) 5; (3) 10; (4) 13; (5) 15; (6) 18; (7) 20; (8) γ^{C} vs. $\hat{X}_2$ curve.

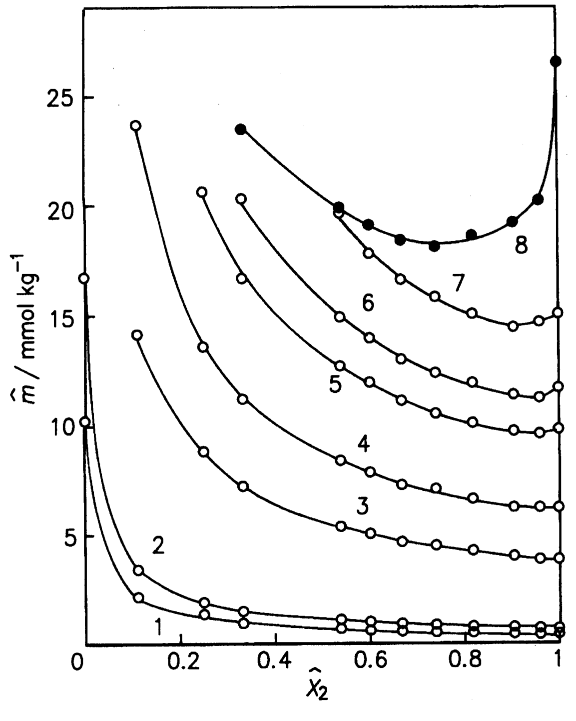

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) $\gamma=68$ mN m^{-1}; (2) 65; (3) 50; (4) 45; (5) 40; (6) 35; (7) 33; (8) $\hat{C}$ vs. $\hat{X}_2$ curve.

concentration and has a shallow minimum at a high concentration. Figure 3 shows the $\hat{m}$ vs. $\hat{X}_2$ curve at constant γ and the $\hat{C}$ vs. $\hat{X}_2$ curve obtained similarly from Fig. 1; the $\hat{m}$ vs. $\hat{X}_2$ curve has a shallow minimum at low γ. It is noted that the $\hat{C}$ vs. $\hat{X}_2$ curve has a remarkable minimum. These minima indicate that there exists the strong interaction between SBAS and OSE molecules in the adsorbed film and micelle.

Miscibility in the Adsorbed Film at a Concentration below the cmc. It has been shown that the total surface density of surfactant $\hat{\Gamma}^{H}$ and the mole fraction of OSE $\hat{X}_2{}^{H}$ are useful to clarify the behavior of the mixed adsorbed film. Here $\hat{\Gamma}^{H}$ and $\hat{X}_2{}^{H}$ are respectively defined by

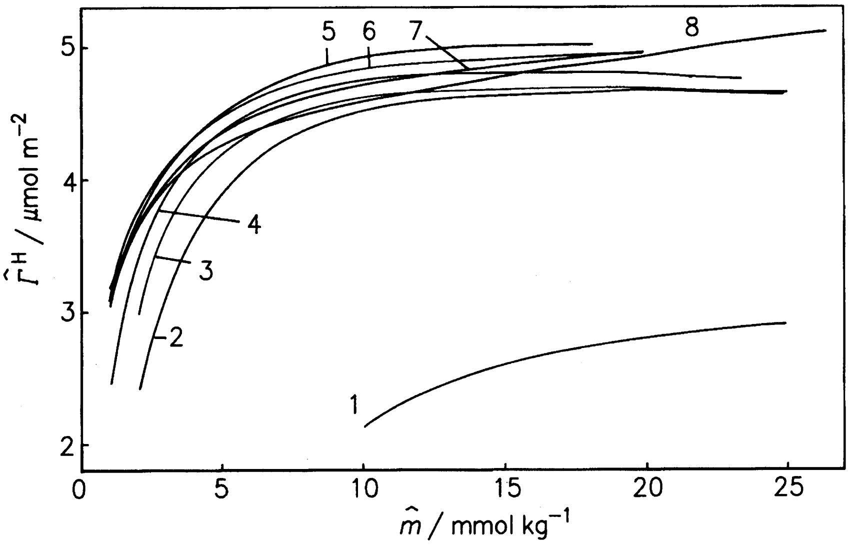

Fig. 4. Total surface density vs. total molality curves at constant composition: (1) $\hat{X}_2=0$; (2) 0.111; (3) 0.250; (4) 0.333; (5) 0.667; (6) 0.740; (7) 0.960; (8) 1.

$$\hat{\Gamma}^H = 2\Gamma_1{}^H + \Gamma_2{}^H \quad (3)$$

and

$$\hat{X}_2^H = \Gamma_2{}^H/\hat{\Gamma}^H, \quad (4)$$

where $\Gamma_1{}^H$ and $\Gamma_2{}^H$ are the surface excess numbers of moles of SBAS and OSE defined with respect to the two dividing planes making simultaneously the surface excess numbers of moles of water and air zero, respectively.[12] The total differential of surface tension is written at constant temperature and pressure as

$$\begin{aligned} d\gamma = & -\left(RT\hat{\Gamma}^H/\hat{m}\right) d\hat{m} \\ & + \left(RT\hat{\Gamma}^H/\hat{X}_1\hat{X}_2\right)\left(\hat{X}_2 - \hat{X}_2^H\right) d\hat{X}_2. \end{aligned} \quad (5)$$

Thus $\hat{\Gamma}^H$ is calculated by applying the following equation to the γ vs. $\hat{m}$ curve illustrated in Fig. 1

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

where the subscript $\hat{X}$ denote $\hat{X}_2$;[4,7] the values are plotted against $\hat{m}$ in Fig. 4. It is interesting to note that, though the adsorption of SBAS is appreciably weak, there exists a $\hat{X}_2$ region where the $\hat{\Gamma}^H$ value of mixture exceeds that of pure OSE. This is probably due to an attractive interaction between OSE and SBAS molecules.

Now let us examine the miscibility of OSE and SBAS in the adsorbed film. By use of the equation derived from Eq. 5

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

the mole fraction of OSE in the adsorbed film is estimated from the $\hat{m}$ vs. $\hat{X}_2$ curves shown in Fig. 3. The $\hat{m}$ vs. $\hat{X}_2{}^H$ curves are depicted together with the corresponding $\hat{m}$ vs. $\hat{X}_2$ curves in Fig. 5. The $\hat{X}_2{}^H$ value is also calculated by substituting the slope of the γ vs. $\hat{X}_2$ curve depicted in Fig. 2 and the $\hat{\Gamma}^H$ value given in Fig. 4 into the equation

$$\hat{X}_2^H = \hat{X}_2 - \left(\hat{X}_1\hat{X}_2/RT\hat{\Gamma}^H\right)\left(\partial\gamma/\partial\hat{X}_2\right)_{T,p,\hat{m}}. \quad (8)$$

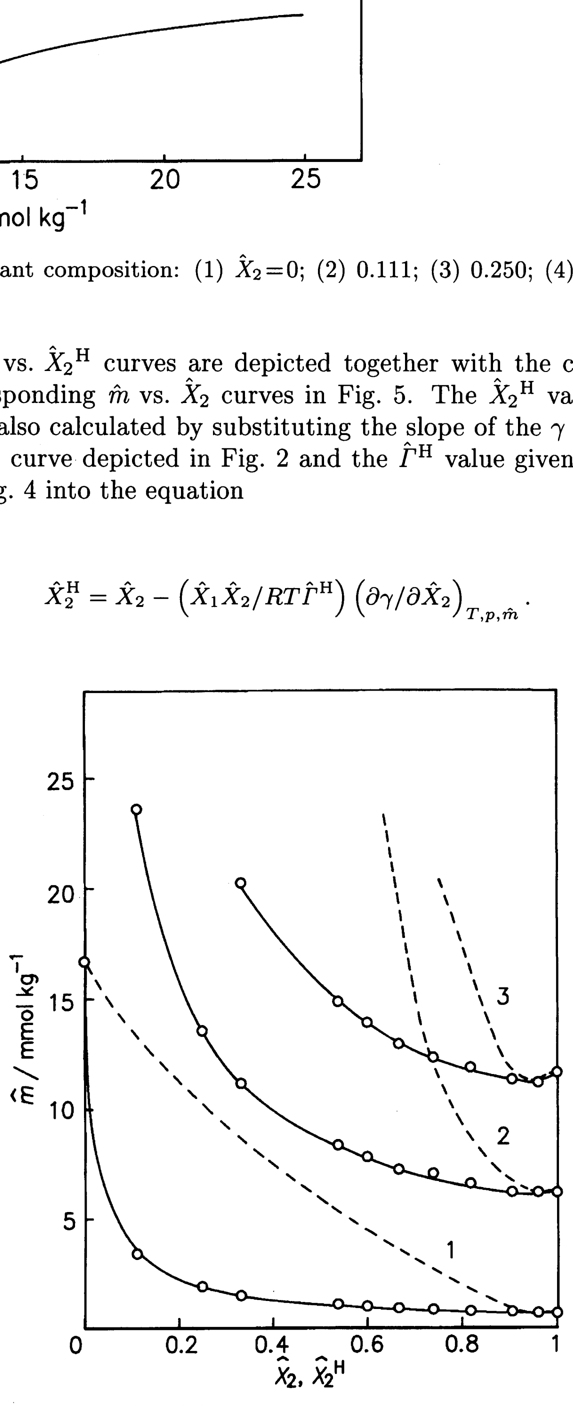

Fig. 5. Total molality vs. composition curves at constant surface tension: (1) γ=65 mN m^{-1}; (2) 45; (3) 38; —— $\hat{m}$ vs. $\hat{X}_2$ curve; - - - $\hat{m}$ vs. $\hat{X}_2{}^H$ curve.

The γ vs. $\hat{X}_2$ and γ vs. $\hat{X}_2{}^{\mathrm{H}}$ curves are shown in Fig. 6. These figures represent the relation between the equilibrium compositions of the solution and adsorbed film. In the adsorbed film, accordingly, SBAS and OSE are completely miscible with each other and OSE is richer than SBAS compared with that in the solution, except for a composition near $\hat{X}_2=1$. Figure 5 shows that the $\hat{m}$ vs. $\hat{X}_2{}^{\mathrm{H}}$ curve of the diagram 1 deviates negatively from the straight line connecting the $\hat{m}$ values of pure dye and OSE and that of the diagram 3 has a shallow minimum. By comparing these results with those of decylammonium chloride (DeAC)–OSE and dodecylammonium chloride (DAC)–OSE systems,[6,7] we can say that SBAS and OSE molecules interact attractively in the adsorbed film. Taking into account that some workers have studied the adsorption and monolayer of dye molecules in connection with dyeing fibers,[13,14] such findings as the abundance of nonionic surfactant and the attractive interaction between surfactant and dye molecules in the adsorbed film may give some clues to an understanding of the role of nonionic surfactant in the dyeing process.

Miscibility in the Micelle and Adsorbed Film at the cmc. To know how the geometry of molecular assembly affects the miscibility of SBAS and OSE molecules, it is of interest to examine the composition in the micelle. The mole fraction of OSE in the micelle is defined by

$$\hat{X}_2^{\mathrm{M}} = N_2/(2N_1 + N_2)\,, \tag{9}$$

where N_1 and N_2 are respectively the excess numbers of molecules of SBAS and OSE with reference to a spherical dividing surface which makes the excess number of molecules of water be zero. The value of $\hat{X}_2{}^{\mathrm{M}}$ is evaluated by using the equation

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

The $\hat{C}$ vs. $\hat{X}_2{}^{\mathrm{M}}$ curve is depicted together with the $\hat{C}$ vs. $\hat{X}_2$ curve in Fig. 7. The phase diagram of micelle formation is seen to have a definite minimum; the micelle abounds in SBAS compared with the solution at a mole fraction above the minimum and in OSE below. Taking into account that the corresponding phase diagram of the DAC–OSE system is similar in shape and that SBAS molecules do not form micelle, we can say that the SBAS and OSE molecules interact attractively with each other in the micellar state.

Furthermore, the mole fraction of OSE $\hat{X}_2{}^{\mathrm{H,C}}$ in the adsorbed film in equilibrium with the micelle at the cmc is evaluated by applying

$$\hat{X}_2^{\mathrm{H,C}} = \hat{X}_2^{\mathrm{M}} - \left(\hat{X}_1\hat{X}_2/RT\hat{\Gamma}^{\mathrm{H,C}}\right)\left(\partial\gamma^{\mathrm{C}}/\partial\hat{X}_2\right)_{T,p} \tag{11}$$

to the γ^{C} vs. $\hat{X}_2$ curve given in Fig. 2. Here $\hat{\Gamma}^{\mathrm{H,C}}$ is the total surface density of mixture estimated by extrapolation to the cmc in Fig. 4. Figure 8 illustrates the γ^{C} vs. $\hat{X}_2{}^{\mathrm{M}}$ and γ^{C} vs. $\hat{X}_2{}^{\mathrm{H,C}}$ curves; the mole fraction of OSE in the micelle is found to be smaller than that in the adsorbed film. Since this diagram is similar in shape to the right part of the maximum of the corresponding one of DAC–OSE system ((Fig. 9) in Ref. 7) and the phase

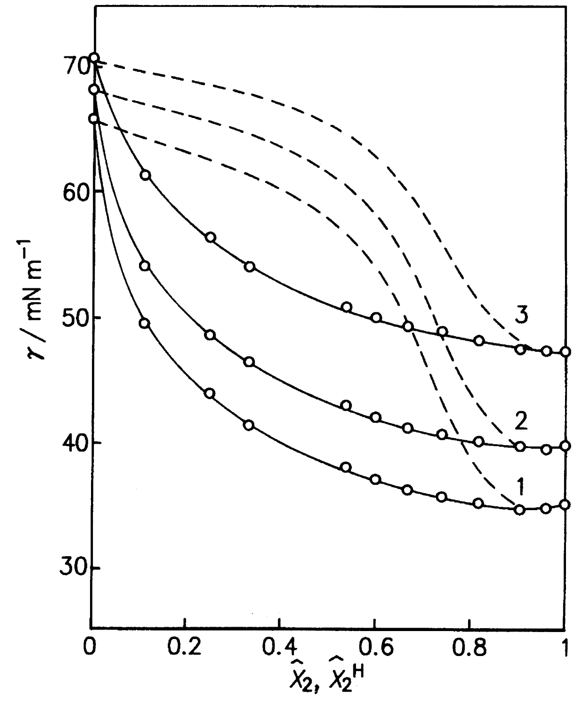

Fig. 6. Surface tension vs. composition curves at constant total molality: (1) $\hat{m}$=15 mmol kg^{-1}; (2) 10; (3) 5; —— γ vs. $\hat{X}_2$ curve; - - - γ vs. $\hat{X}_2{}^{\mathrm{H}}$ curve.

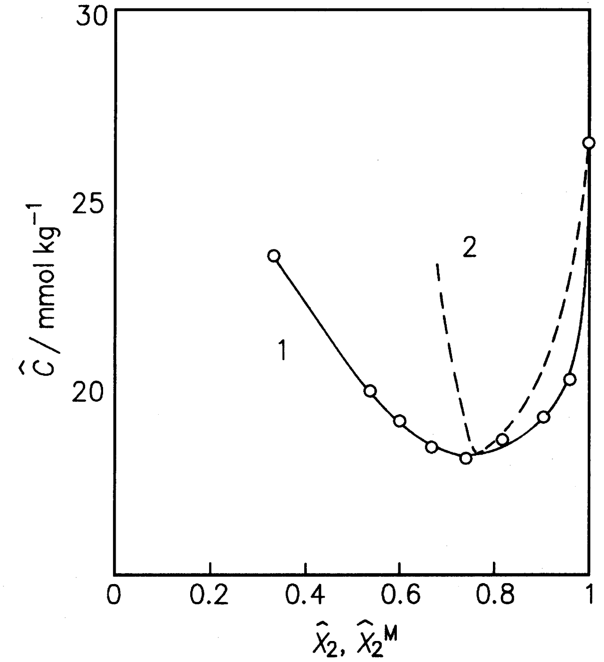

Fig. 7. Critical micelle concentration vs. composition curves: (1) $\hat{C}$ vs. $\hat{X}_2$ curve; (2) $\hat{C}$ vs. $\hat{X}_2{}^{\mathrm{M}}$ curve.

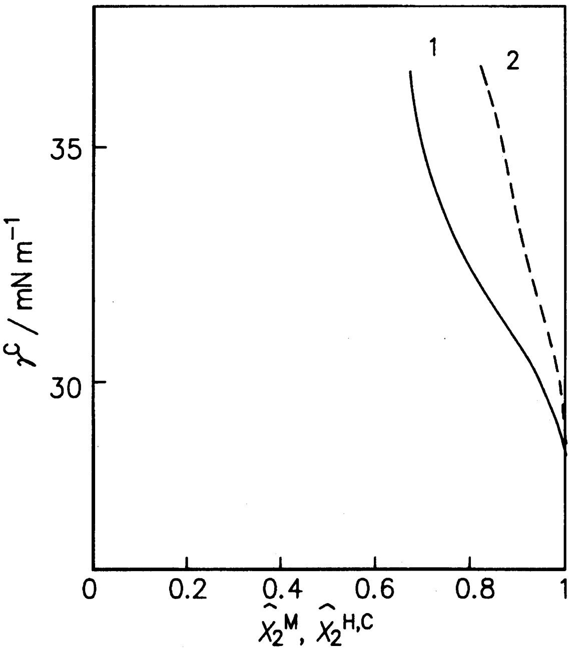

Fig. 8. Surface tension at the critical micelle concentration vs. composition curves: (1) γ^C vs. $\hat{X}_2{}^M$ curve; (2) γ^C vs. $\hat{X}_2{}^{H,C}$ curve.

diagram of micelle formation has a minimum sharper than that of adsorption, the interaction between SBAS and OSE molecules is more attractive in the spherical micelle than in the plane adsorbed film.

It is said that the miscibility between SBAS and OSE molecules in the adsorbed film and micelle is greatly affected by the differences in abilities of adsorption and micelle formation between SBAS and OSE and by the attractive interaction. Further it is said that nonionic surfactant plays an important role in dyeing process as a levelling agent. The surface tension measurement and thermodynamic consideration are now in progress with respect to other combinations of dyes and surfactants.

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