Interaction of Sodium 4′-(Butylamino)azobenzene-4-sulfonate with Octyl Methyl Sulfoxide in Adsorbed Film and Micelle

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The surface tension of the aqueous solution of sodium 4′-(butylamino)azobenzene-4-sulfonate (SBAS) and octyl methyl sulfoxide (OMS) mixture was measured as a function of the total molality at various compositions and at 298.15 K under atmospheric pressure. The experimental results were analyzed by applying the thermodynamic relations. The phase diagrams of adsorption and micelle formation were found to suggest that SBAS and OMS molecules interact attractively with each other to form a negative azeotropic mixture in the adsorbed film at a low surface tension and in the micelle. These findings were qualitatively similar to those of the system of SBAS and 2-(octylsulfinyl)ethanol (OSE) and confirmed our conclusion that the strong interaction of dye and nonionic surfactant molecules at the interface may be the one of reasons why a nonionic surfactant acts as the leveling agent in dyeing process.

The two types of mechanisms have been proposed to explain the leveling action of surfactant.[1—3] The one is the competitive adsorption of dye and surfactant on fiber provided by the mixture of acid dye and anionic surfactant. The other is the complex formation of dye and surfactant provided by the acid dye and nonionic surfactant mixture.

On the other hand we have suggested that the surface adsorption behavior from the aqueous solutions of dye and surfactant mixtures well explains the leveling action of surfactants in the dyeing process; the first case such as Orange II and sodium dodecyl sulfate mixture is explicable by the weak interaction between acid dye and anionic surfactant molecules which results in an appreciable decrease of the mole fraction of dye in the adsorbed film and micelle compared with the bulk solution.[4] The second case such as sodium 4′-(butylamino)azobenzene-4-sulfonate (SBAS) and 2-(octylsulfinyl)ethanol (OSE) mixture is explicable by the attractive interaction between acid dye and nonionic surfactant molecules which is so strong that the mixture forms a negative azeotrope in the adsorbed film at a low surface tension and in the micelle.[5]

Our view on the first case has been further confirmed by using the mixture of Metanil Yellow and sodium dodecyl sulfate.[4] Now it is required to make sure the view on the second case. For this purpose, the mixture of SBAS and octyl methyl sulfoxide (OMS) is chosen and studied by measuring the surface tension and by analyzing the results thermodynamically.

Experimental

Octyl methyl sulfoxide (OMS) was synthesized according to the method in the literature[6] and purified by repeated recrystallization from ethanol and petroleum ether. Sodium 4′-(butylamino)azobenzene-4-sulfonate (SBAS) was synthesized and purified according to the previously reported method.[7] Their purities were checked by elemental analysis. No minimum was detected on the surface tension vs. concentration curve around the critical micelle concentration (cmc) of OMS.

The surface tension was measured by the drop volume method within the error of 0.05 $\mathrm{mN\,m^{-1}}$ at 298.15 K under atmospheric pressure.[8] Water was distilled triply from alkaline permanganate solution.

Results and Discussion

The total molality $\hat{m}$ and the mole fraction of OMS $\hat{X}_2$ of SBAS–OMS mixture were employed as the experimental variables at constant temperature and pressure. Taking the dissociation of SBAS molecules into consideration,[9—11] 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 OMS, respectively. The surface tension γ was plotted against $\hat{m}$ at fixed compositions in Fig. 1; the total molality $\hat{C}$ and surface tension γ^c at the critical micelle concentration (cmc) were determined.

To elucidate the complicated dependence of γ on $\hat{m}$ and $\hat{X}_2$ in Fig. 1, the two types of plots are useful; the one is the γ vs. $\hat{X}_2$ curves at constant $\hat{m}$ drawn together with the γ^c vs. $\hat{X}_2$ curve in Fig. 2 and the other is the $\hat{m}$ vs. $\hat{X}_2$ curves at constant γ drawn together with the $\hat{C}$ vs. $\hat{X}_2$ curve in Fig. 3. It is seen that the γ value in a low $\hat{m}$ region and the $\hat{m}$ value in a high γ region decrease with increasing $\hat{X}_2$ while the γ vs. $\hat{X}_2$ curve in a high $\hat{m}$ region and the $\hat{m}$ vs. $\hat{X}_2$ curve at a low γ region have a shallow minimum. Furthermore, the $\hat{C}$ value passes through a distinct minimum, while the γ^c value decreases monotonously with $\hat{X}_2$. These results will be considered below in connection with the attractive interaction between SBAS and OMS molecules in the adsorbed film and micelle.

Now let us analyze the results given in Figs. 1, 2,

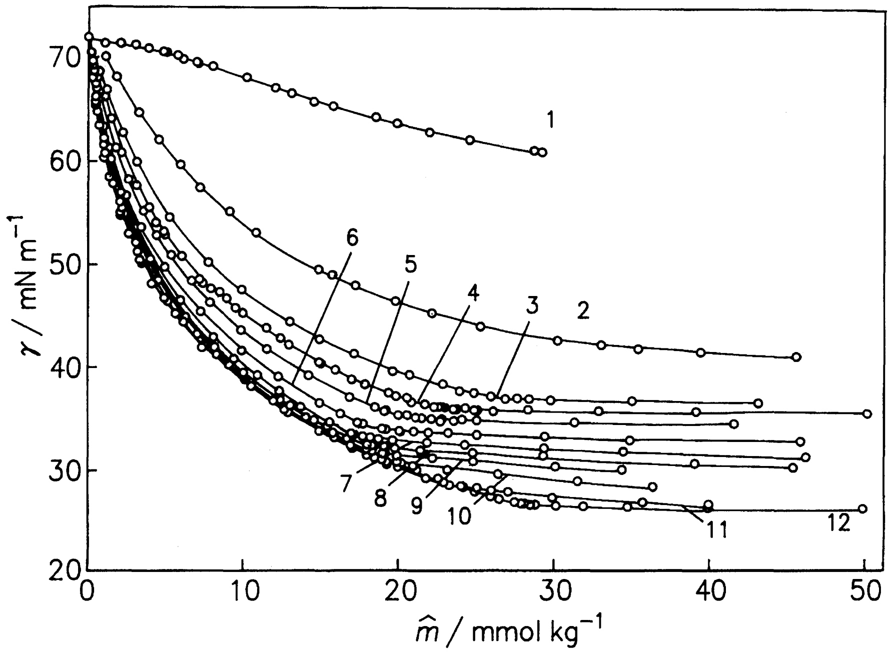

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) $\hat{X}_2=0$; (2) 0.0991; (3) 0.248; (4) 0.333; (5) 0.419; (6) 0.550; (7) 0.667; (8) 0.747; (9) 0.820; (10) 0.905; (11) 0.980; (12) 1.

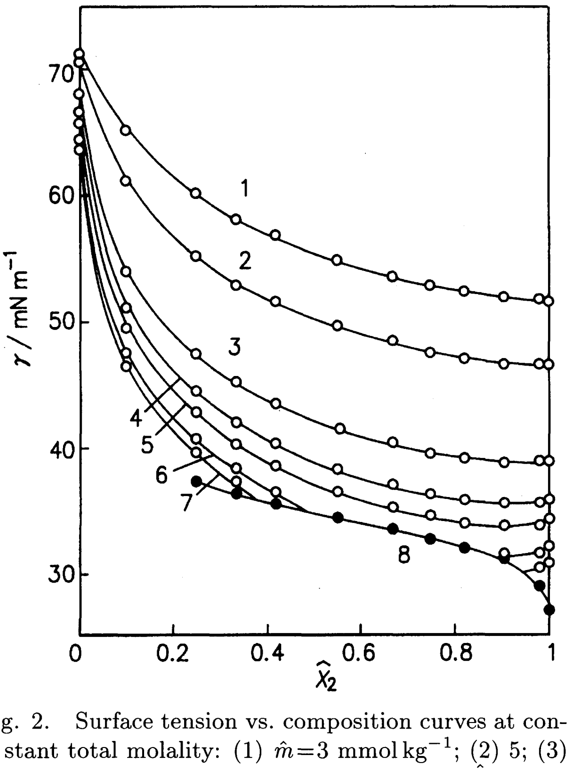

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) $\hat{m}=3$ mmol kg^{-1}; (2) 5; (3) 10; (4) 13; (5) 15; (6) 18; (7) 20; (8) γ^{c} vs. $\hat{X}_2$.

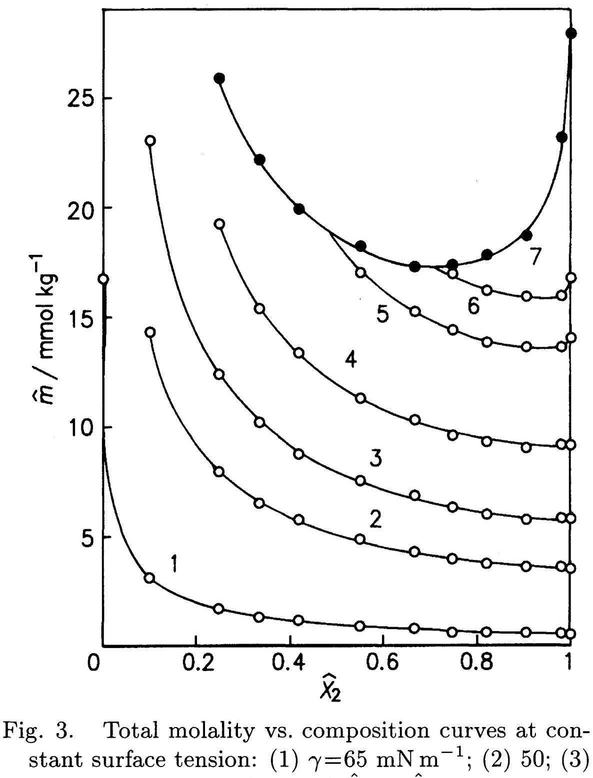

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) γ=65 mN m^{-1}; (2) 50; (3) 45; (4) 40; (5) 35; (6) 33; (7) $\hat{C}$ vs. $\hat{X}_2$.

and 3 by use of the thermodynamics developed previously.[10,12] The miscibility of SBAS and OMS is disclosed by the phase diagram of adsorption which provides the information on the molecular interaction in the adsorbed film. The diagram is constructed by using the mole fraction of OMS in the adsorbed film $\hat{X}_2^{\mathrm{H}}$ defined by

$$\hat{X}_2^{\mathrm{H}} = \Gamma_2^{\mathrm{H}}/(2\Gamma_1^{\mathrm{H}} + \Gamma_2^{\mathrm{H}}), \tag{3}$$

where Γ_1^{H} and Γ_2^{H} are the surface excess numbers of moles of SBAS and OMS, respectively; the $\hat{X}_2^{\mathrm{H}}$ value is calculated by applying the relation

$$\hat{X}_2^{\mathrm{H}} = \hat{X}_2 - (\hat{X}_1\hat{X}_2/\hat{m})(\partial\hat{m}/\partial\hat{X}_2)_{T,p,\gamma} \quad (4)$$

to the $\hat{m}$ vs. $\hat{X}_2$ curves given in Fig. 3.

In Fig. 4 are shown the diagrams at three γ values. It is clearly seen that OMS molecules are completely miscible with SBAS molecules in the adsorbed film and abound in it compared with the bulk solution. It should be noted that the $\hat{m}$ vs. $\hat{X}_2^{\mathrm{H}}$ curve deviates negatively from the straight line connecting the $\hat{m}$ values at $\hat{X}_2=0$ and 1. Furthermore, looking more closely at the diagram 3 in Fig. 4, we notice that the adsorbed film is rich in the less surface active SBAS molecules in the composition region near $\hat{X}_2=1$. This corresponds to the negative azeotropy of three dimensional phase diagram. These findings suggest that the attractive interaction between different species is stronger than that between same species. This statement is further confirmed by the total surface density of surfactant $\hat{\Gamma}^{\mathrm{H}}$ $(=2\Gamma_1^{\mathrm{H}}+\Gamma_2^{\mathrm{H}})$ which is calculated by use of the equation

$$\hat{\Gamma}^{\mathrm{H}} = -(\hat{m}/RT)(\partial\gamma/\partial\hat{m})_{T,p,\hat{X}_2} \quad (5)$$

and plotted against $\hat{m}$ in Fig. 5; although the $\hat{\Gamma}^{\mathrm{H}}$ value of dye itself is rather small, the $\hat{\Gamma}^{\mathrm{H}}$ value of mixture is larger than that of pure OMS in a high $\hat{m}$ and high $\hat{X}_2$ region.

To obtain information on the molecular interaction in the oriented state, the miscibility of molecules in the micelle is also valuable; it is successfully clarified by evaluating the composition in the micelle. The mole fraction of OMS in the micelle is defined by

$$\hat{X}_2^{\mathrm{M}} = N_2^{\mathrm{M}}/(2N_1^{\mathrm{M}} + N_2^{\mathrm{M}}), \quad (6)$$

where N_1^{M} and N_2^{M} are respectively the excess numbers of molecules of SBAS and OMS per micelle particle with reference to a spherical dividing surface which makes the excess number of molecules of water zero.[11—13] The value of $\hat{X}_2^{\mathrm{M}}$ is evaluated by applying the equation

$$\hat{X}_2^{\mathrm{M}} = \hat{X}_2 - (\hat{X}_1\hat{X}_2/\hat{C})(\partial\hat{C}/\partial\hat{X}_2)_{T,p} \quad (7)$$

to the $\hat{C}$ vs. $\hat{X}_2$ curve in Fig. 3 and depicted in the form of the phase diagram of micelle formation in Fig. 6. By adding SBAS to the aqueous solution of OMS, the cmc is greatly decreased, passes through a minimum, and then is sharply increased. At a mole fraction above the minimum point, micelle particles are enriched in SBAS molecules, which do not form micelles solely, compared

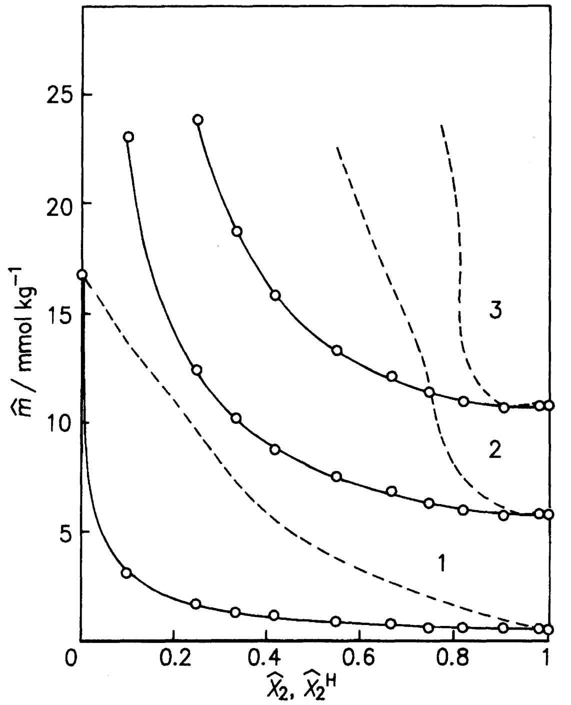

Fig. 4. Total molality vs. composition curves at constant surface tension: (1) γ=65 mN m^{-1}; (2) 45; (3) 38; (—) $\hat{m}$ vs. $\hat{X}_2$; (---) $\hat{m}$ vs. $\hat{X}_2^{\mathrm{H}}$.

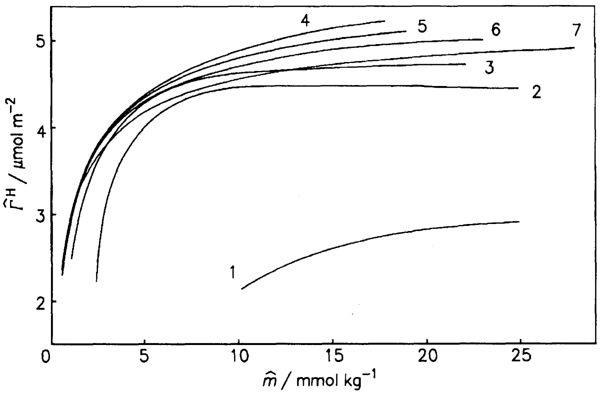

Fig. 5. Total surface density vs. total molality curves at constant composition: (1) $\hat{X}_2=0$; (2) 0.0991; (3) 0.333; (4) 0.747; (5) 0.905; (6) 0.980; (7) 1.

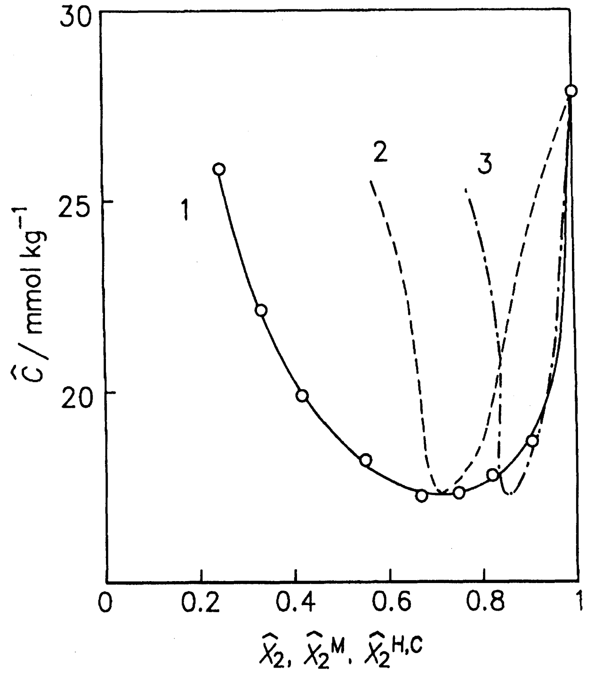

Fig. 6. Critical micelle concentration vs. composition curves: (1) $\hat{C}$ vs. $\hat{X}_2$; (2) $\hat{C}$ vs. $\hat{X}_2^{\mathrm{M}}$; (3) $\hat{C}$ vs. $\hat{X}_2^{\mathrm{H,C}}$.

with the bulk solution. Therefore, it can be said that SBAS and OMS molecules attractively interact with each other in the micelle as in the adsorbed film.

Furthermore, the mole fraction of OMS in the adsorbed film at the cmc $\hat{X}_2^{\mathrm{H,C}}$ is evaluated by using the equation

$$\hat{X}_2^{\mathrm{H,C}} = \hat{X}_2^{\mathrm{M}} - (\hat{X}_1\hat{X}_2/RT\hat{\Gamma}^{\mathrm{H,C}})(\partial\gamma^{\mathrm{C}}/\partial\hat{X}_2)_{T,p}, \quad (8)$$

where $\hat{\Gamma}^{\mathrm{H,C}}$ is the total surface density of mixture at the cmc estimated from Fig. 5. The $\hat{C}$ vs. $\hat{X}_2^{\mathrm{H,C}}$ curve is also drawn in Fig. 6; the deep minimum is also observed at a high surface composition. To make clearer the relation between the compositions of the micelle and the adsorbed film at the cmc, the γ^{c} vs. $\hat{X}_2^{\mathrm{M}}$ and γ^{c} vs. $\hat{X}_2^{\mathrm{H,C}}$ curves are depicted in Fig. 7. By taking into account that the micelle is richer in SBAS molecules than the adsorbed film, it is said that the interaction between SBAS and OMS molecules is more attractive in the spherical micelle than in the plane adsorbed film.[11)]

The results of the SBAS and OMS mixture are qualitatively similar to those of the SBAS and OSE mixture.[5)] Since SBAS is the common component, it is interesting to examine the difference in the miscibility in the adsorbed film and micelle between the two systems. In Fig. 8, the mole fractions of OMS and OSE in the adsorbed film and micelle at the cmc are plotted against $\hat{X}_2$. It is seen that the difference is appreciable, though small. Judging from the facts that the adsorbed film and micelle of SBAS–OMS system are richer in less surface active SBAS molecules than those of the SBAS–OSE system at a given $\hat{X}_2$ and that the minimum of the $\hat{C}$ vs. $\hat{X}_2$ curve of the former is deeper than that of the latter, the molecular interaction between dye and surfactant molecules is stronger in the SBAS–OMS system than in the SBAS–OSE system.

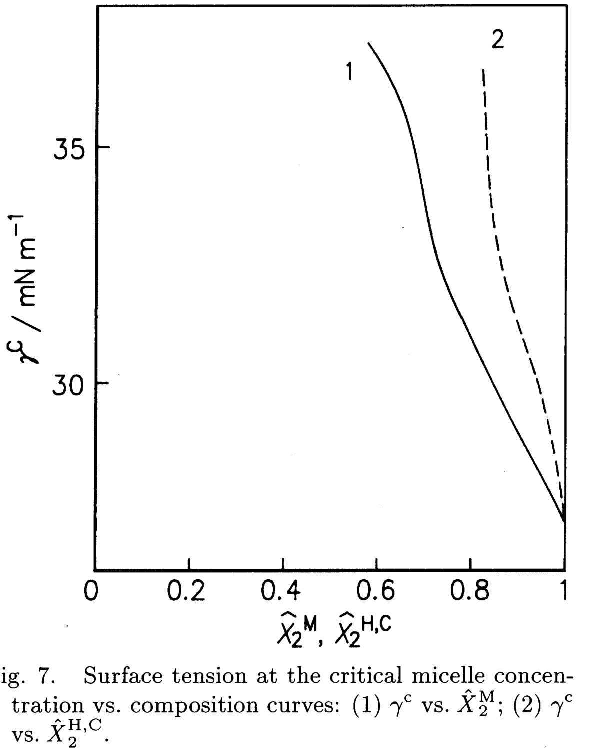

Fig. 7. Surface tension at the critical micelle concentration vs. composition curves: (1) γ^{c} vs. $\hat{X}_2^{\mathrm{M}}$; (2) γ^{c} vs. $\hat{X}_2^{\mathrm{H,C}}$.

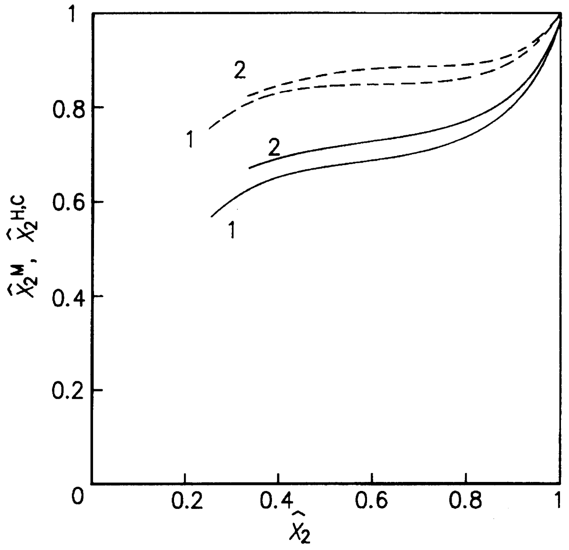

Fig. 8. Composition in the micelle (—) and composition in the adsorbed film (- - -) vs. composition curves at the critical micelle concentration: (1) SBAS–OMS system; (2) SBAS–OSE system.

Furthermore, the negative azeotrope has been found in the adsorbed film and micelle of sodium-4′-(diethylamino)azobenzene-4-sulfonate and OSE mixture.[14)] By considering these findings, the functional groups in the dye and the sulfinyl group in the nonionic surfactant are concluded to play a significant role in the strong interaction between them. Therefore the interaction at the interface may be the one of reasons why a nonionic surfactant acts as the leveling agent in dyeing process.

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