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Miscibility of 1-Octanol and 2-(Octylsulfinyl)ethanol in the Adsorbed Film and Micelle

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The surface tension of the aqueous solution of 1-octanol and 2-(octylsulfinyl)ethanol (OSE) mixture was measured as a function of the total molality of surfactants and the composition of OSE in the total surfactants at 298.15 K under atmospheric pressure. It was observed that 1-octanol molecules form mixed micelles with OSE molecules in the composition range above 0.850. The corresponding composition in the mixed adsorbed film was evaluated numerically by applying the thermodynamic relations developed previously. It was found that the surfactant molecules mix with each other in all proportions in the adsorbed film and the composition in the adsorbed film is smaller than that in the solution. Further, the adsorbed film was found to be richer in 1-octanol than the micelle at the critical micelle concentration (cmc). This behavior was attributed to the fact that 1-octanol is more surface active than OSE though it does not form the micelle.

In our previous papers, the thermodynamics of adsorption[1,2] and micelle formation[3] of surfactants has been developed on the basis of the excess thermodynamic quantities and extended so as to be applicable to surfactant mixtures.[4,5] Further,the relation among the compositions of bulk solution, adsorbed film, and micelle has been discussed for mixed systems of cationic surfactants[5-8] and that of nonionic surfactants.[9] In these systems, the surfactants form their individual micelles and their mixtures form mixed micelles over the whole composition region. Now it is interesting to examine whether a mixture of two surface active components, of which one (component 1) does not form micelle, mix in the micellar state and how the composition of mixed micelle is correlated with that of mixed adsorbed film.

To obtain useful information about the miscibility of surfactants in such a system, we choose the 1-octanol-2-(octylsulfinyl)ethanol (OSE) mixture for reasons that (i) the surfactants are different only in the chemical structure of head group from each other, (ii) their adsorption and micelle formation have been investigated in our previous papers,[10,11] and (iii) the effect of alcohol on their behavior has been discussed by many workers from the point of view of a mixed solvent or an organic additive.[12-18] In the present study, the alcohol molecules are treated as surfactant molecules. The surface tension is measured as a function of the total concentration and composition of the mixture near the critical micelle concentration (cmc) at constant temperature under atmospheric pressure.

Experimental

1-Octanol (Nacalai Tesque's guaranteed reagent) was fractionally distilled under reduced pressure. Its purity (>99%) was checked by a gas-liquid chromatography. 2-(Octylsulfinyl)ethanol was synthesized and purified by the method described previously.[10] Its purity checked by a gas-liquid chromatography was better than 99%. No minimum was observed on the surface tension vs. concentration curve of 2-(octylsulfinyl)ethanol. Water was triply distilled from dilute alkaline permanganate solution.

The surface tension of aqueous solution was measured by the drop volume technique at 298.15 K under atmospheric pressure.[19] The experimental error was within 0.05 mN m^{-1}. The temperature was kept constant within 0.01 K by immersing the measuring cell in a thermostat.

Results and Discussion

In order to examine the miscibility of surfactants in the adsorbed film and micelle, it is useful to adopt the total molality m and composition of surfactant mixture X_2 in the aqueous solution defined, respectively, by[5-9]

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

and

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

at constant temperature T and pressure p. Here m_1

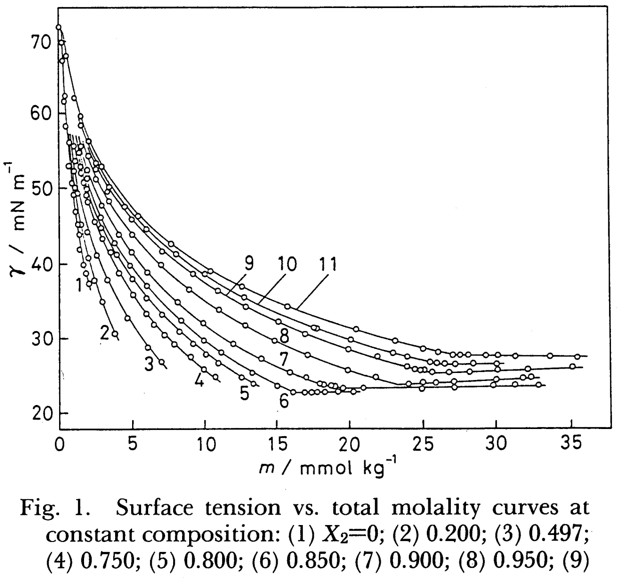

Fig. 1. Surface tension vs. total molality curves at constant composition: (1) X_2=0; (2) 0.200; (3) 0.497; (4) 0.750; (5) 0.800; (6) 0.850; (7) 0.900; (8) 0.950; (9) 0.980; (10) 0.990; (11) 1.

and m_2 represent the molalities of 1-octanol and OSE, respectively. The surface tension γ of the aqueous solution of the mixture was measured as a function of m at fixed values of X_2 at 298.15 K under atmospheric pressure.

The surface tension measured is plotted against the total molality at constant compositions in Fig. 1. The γ value decreases with increasing m and varies regularly with X_2. When X_2 is larger than about 0.850, a break is observed on the γ vs. m curve and its concentration is referred to as the critical micelle concentration (cmc). However, the break is not observed when X_2 is smaller than about 0.800, because the solution of mixture separates into two phases. Therefore it is concluded that such a mixture (X_2<0.800) does not form micelles in the solution. Figures 2 and 3 show the variation of γ with X_2 at a given m and that of m with X_2 at a given γ obtained from Fig. 1, respectively. The surface tension at the cmc γ^C and the cmc C are also drawn in Figs. 2 and 3, respectively. Both the γ^C and C values decrease with increasing the composition of 1-octanol. When 1-octanol is regarded as an additive to the aqueous solution of OSE, the molality of OSE m_2^C at the break point is usually defined as the cmc. In Fig. 4, m_2^C is plotted against the molality of 1-octanol m_1; m_2^C is seen to decrease with increasing m_1, which is apparently similar in shape to the C vs. X_2 curve. However, as will be shown later, the C vs. X_2 curve gives useful information about the miscibility of surfactants in the mixed micelle.

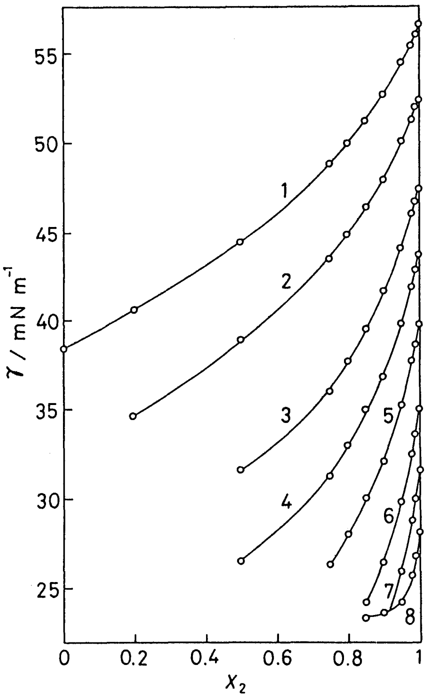

Fig. 2. Surface tension vs. composition curves at constant total molality: (1) m=2 mmol kg^{-1}; (2) 3; (3) 5; (4) 7; (5) 10; (6) 15; (7) 20; (8) γ^C vs. X_2.

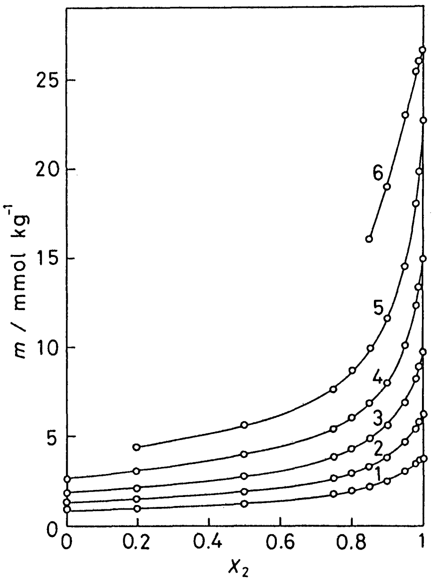

Fig. 3. Total molality vs. composition curves at constant surface tension: (1) γ=50 mN m^{-1}; (2) 45; (3) 40; (4) 35; (5) 30; (6) C vs. X_2.

Miscibility in the Adsorbed Film below the cmc. First we examine the adsorption of the mixture at concentrations below the cmc in terms of the total surface density Γ^H and the composition of OSE in the mixed adsorbed film X_2^H. Here Γ^H and X_2^H are defined, respectively, by

$$\Gamma^H = \Gamma_1^H + \Gamma_2^H \tag{3}$$

and

$$X_2^H = \Gamma_2^H / \Gamma^H, \tag{4}$$

where Γ_i^H is the surface excess number of moles per unit area of component i with respect to the two dividing planes.[1,2]

The numerical values of Γ^H were estimated by applying the equation[9]

$$\Gamma^H = -(m/RT)\,(\partial\gamma/\partial m)_{T,p,X_2} \tag{5}$$

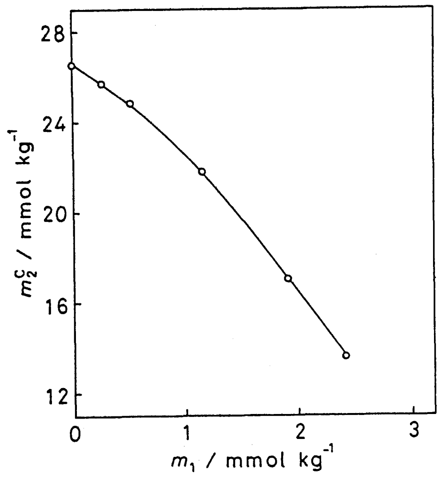

Fig. 4. Critical micelle concentration of OSE vs. molality of 1-octanol curve.

to the curves shown in Fig. 1; they are plotted against m at constant X_2 in Fig. 5. The Γ^H value increases with increasing m and reaches the saturated one at a concentration near the cmc. However, when the aqueous solution is enriched in OSE, the Γ^H vs. m curve rises steeply. On the other hand, the value of Γ^H is seen to decrease remarkably with increasing X_2 at a given m. These findings suggest that there is difference in composition between the adsorbed film and the bulk solution. Now it is necessary to estimate the composition of OSE in the mixed adsorbed film.

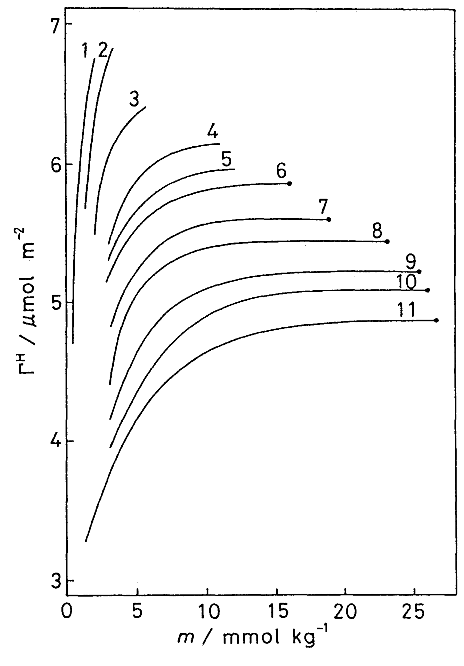

Fig. 5. Total surface density vs. total molality curves at constant composition: (1) X_2=0; (2) 0.200; (3) 0.497; (4) 0.750; (5) 0.800; (6) 0.850; (7) 0.900; (8) 0.950; (9) 0.980; (10) 0.990; (11) 1; (●) total surface density at the cmc $\Gamma^{H,C}$.

The X_2^H values at constant γ can be evaluated with the aid of the equation derived for the mixture of two nonionic surfactants in our previous paper:[9]

$$X_2^H = X_2 - (X_1X_2/m)\,(\partial m/\partial X_2)_{T,p,\gamma}. \qquad (6)$$

The values calculated by applying Eq. 6 to the curves given in Fig. 3 are represented diagrammatically in the form of the m vs. X_2^H curves together with the corresponding m vs. X_2 curves in Fig. 6. The X_2^H value is significantly smaller than the X_2 value over the whole range of composition. Since the diagrams are similar in shape to a cigar, the surfactant molecules may mix with each other in all proportions in the adsorbed film.[4–9,20] The value of X_2^H at constant m can also be obtained from the γ vs. X_2 curve given in Fig. 2 by use of the equation[9]

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

The results are depicted in the form of the γ vs. X_2^H curves together with the corresponding γ vs. X_2 curves in Fig. 7. The diagrams are essentially similar to those shown in Fig.6.

Close examination of Figs. 6 and 7 shows that the gap between the compositions of aqueous solution and adsorbed film varies with the surface tension at a fixed total molality and with the total molality at a fixed surface tension. Figure 8 shows the X_2—X_2^H vs. X_2 curve at 40 mN m^{-1}. This difference X_2—X_2^H reaches the maximum value, which is about 0.35, at X_2=about 0.8. In order to gain some information about the influence of chemical structure of surfactant molecules on their miscibilty in the adsorbed film, the corresponding curve of 2-(decylsulfinyl)ethanol (DeSE)-OSE mixture[9] is also drawn in Fig. 8. Both

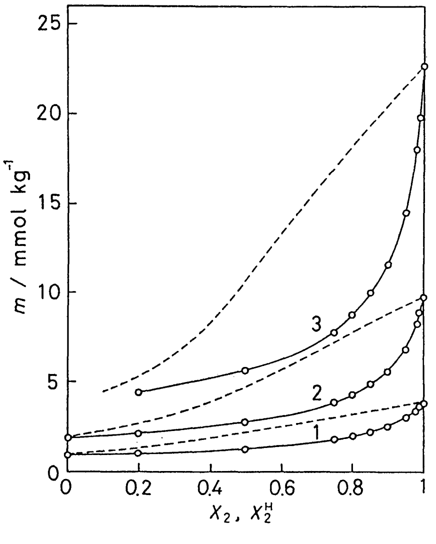

Fig. 6. Total molality vs. composition curves at constant surface tension: (1) γ=50 mN m^{-1}; (2) 40; (3) 30; (——) X_2; (----) X_2^H.

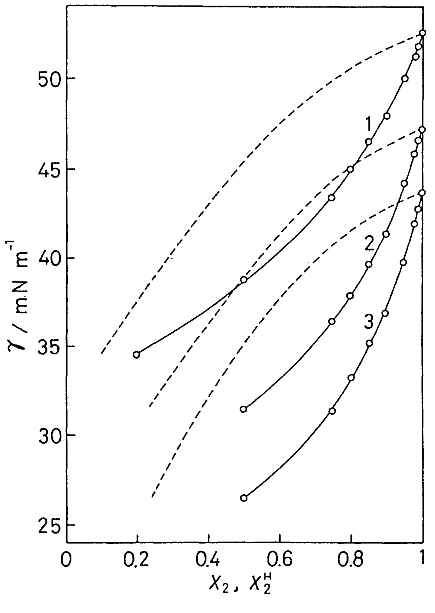

Fig. 7. Surface tension vs. composition curves at constant total molality: (1) m=3 mmol kg^{-1}; (2) 5; (3) 7; (——) X_2; (----) X_2^H.

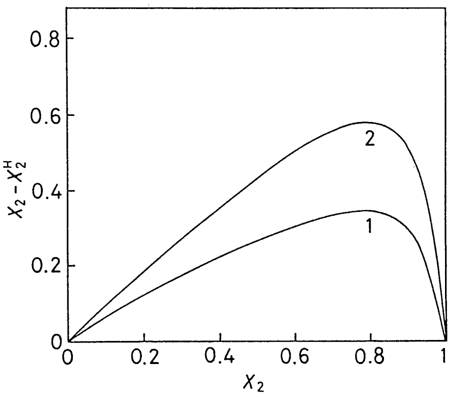

Fig. 8. Composition differences $X_2 - X_2^H$ vs. composition curves at γ=40 mN m^{-1}: (1) 1-octanol-OSE system; (2) DeSE-OSE system.

the curves have maxima at similar bulk compositions but the values at the maxima are different from one another. The difference in the hydrocarbon chain length of surfactant appears to have a remarkable influence on the miscibility in the mixed adsorbed film.

Miscibility in the Adsorbed Film and Micelle at the cmc. As seen above, the adsorbed film is richer in 1-octanol molecules than the solution. Now it is interesting to examine whether 1-octanol molecules are incorpolated into the micelle of OSE though they do not form micelle. Let us introduce the composition of OSE in the micelle X_2^M defined in a similar manner as that in the adsorbed film by

$$X_2^M = N_2^M/(N_1^M + N_2^M), \tag{8}$$

where N_i^M is the excess number of molecules of surfactant i in one mixed micelle particle with reference to the spherical dividing surface.[4] The value of X_2^M is calculated by applying the following equation[4,9] to the C vs. X_2 curve given in Fig. 3:

$$X_2^M = X_2 - (X_1X_2/C)(\partial C/\partial X_2)_{T,p}. \tag{9}$$

The C vs. X_2^M curve obtained are shown together with the C vs. X_2 curve in Fig. 9. 1-Octanol molecules form mixed micelle with OSE molecules and are preferentially incorporated into the micelle. Further the X_2^M value is given in the form of the γ^C vs. X_2^M and γ^C vs. X_2 curves in Fig. 10. This diagram is informative to understand qualitatively the change of γ value with the total molality in the concentration region above the cmc; that is, the γ value is expected to increase gradually with m in this concentration region. This is in accord with the behavior of the γ vs. m curve observed in Fig. 1.

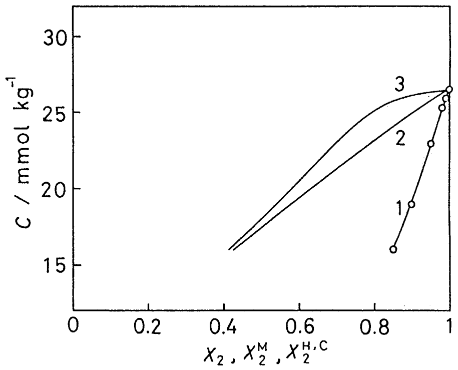

Fig. 9. Critical micelle concentration vs. composition curves: (1) C vs. X_2; (2) C vs. X_2^M; (3) C vs. $X_2^{H,C}$.

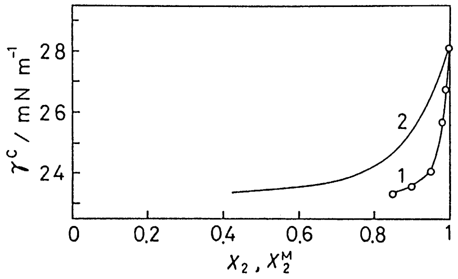

Fig. 10. Surface tension at the cmc vs. composition curves: (1) γ^C vs. X_2; (2) γ^C vs. X_2^M.

Finally we direct our attention to the difference in composition between the micelle and the adsorbed film. The composition in the adsorbed film existing in equilibrium with the micelle at the cmc $X_2^{H,C}$ is evaluated by making use of the relation[9]

$$X_2^{H,C} = X_2^M - (X_1X_2/RT\Gamma^{H,C})(\partial\gamma^C/\partial X_2)_{T,p}, \tag{10}$$

where $\Gamma^{H,C}$ is the total surface density of the mixture at the cmc. The $X_2^{H,C}$ values calculated by using the γ^C vs. X_2 curve given in Fig. 2 and the X_2^M values given in Fig. 9 are illustrated in the form of the C vs. $X_2^{H,C}$ plot in Fig. 9. The adsorbed film at the cmc is enriched in 1-octanol compared with the micelle as shown in Fig. 9. Taking into account that the diagram of Fig. 9 is partly similar to those observed in the dodecylammonium chloride (DAC)-decylammonium chloride (DeAC), decylammonium bromide (DeAB)-DeAC, and DeSE-OSE systems,[6,8,9] this behavior is attributable to the fact that 1-octanol is more surface active than OSE although it does not form a micelle.

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