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Mixed Adsorbed Film of 2-(Octylsulfinyl)ethanol with Decylammonium Chloride at Water/Air Interface

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The surface tension of the aqueous solution of 2-(octylsulfinyl)ethanol and decylammonium chloride mixture has been measured by changing the total molality and composition of surfactants at 298.15 K under atmospheric pressure. It has been observed that the surface tension decreases with increasing the total molality at a constant composition and with decreasing the composition of decylammonium chloride at a constant total molality. Further the surface tension *vs.* total molality curve has been found to have a break point at a relatively low concentration. The thermodynamic equations have been developed so as to be applicable to the adsorption of nonionic-ionic mixture and used to calculate the surface density and the surface composition. It has been shown that the surface density *vs.* molality curve has the discontinuous change caused by the transition from a gaseous to an expanded film. By drawing the two-dimensional phase diagram and comparing it with the diagrams of the ionic-ionic surfactant mixtures, it has been proved that the shape of the phase diagram is affected greatly by the difference in the surface activity between the two surfactants.

The adsorption at water/air interface in a relatively dilute concentration region has been investigated in our laboratory for various types of surfactants[1,2] and cationic–cationic surfactant mixtures such as dodecylammonium chloride (DAC)–decylammonium chloride (DeAC)[3] and dodecyltrimethylammonium chloride (DTAC)–DeAC.[4] It has been observed that the surface tension *vs.* concentration curve has a break point at which a gaseous and an expanded film coexist in equilibrium. As for the ionic surfactant mixtures, we have derived the relation between compositions of the adsorbed film and the bulk phase and shown that the phase diagrams are useful in describing the miscibility of surfactants and phase transition in the mixed adsorbed films. Some studies on cationic–nonionic surfactant mixtures have been carried out from the viewpoints of their mixed micelle formation[5,6] or of their adsorption at water/air interface.[7] In the present study, 2-(octylsulfinyl)ethanol (OSE) is used as the nonionic surfactant for the following reasons; (a) the synthesis and purification of OSE is relatively easy,[8] (b) the adsorption behavior of OSE in the dilute concentration region has been already reported[2] and (c) information about the solution properties of OSE is available.[9,10] By measuring the surface tension of the aqueous solution of OSE–DeAC mixture and applying the thermodynamic equations, which are developed in the present paper, we consider the adsorption of surfactant mixtures from their aqueous solution at the solution/air interface.

Experimental

2-(Octylsulfinyl)ethanol and decylammonium chloride were synthesized and purified by the methods described previously.[1,11] Their purities were checked by the elementary analysis and guaranteed by the absence of minimum near their critical micelle concentration of the surface tension *vs.* concentration curves at 298.15 K. Water was triply distilled from alkaline permanganate solution. The surface tension was measured by the drop volume technique described in our previous paper.[1] The temperature was kept constant at 298.15 K by immersing the measuring cell in a thermostated water bath. The error estimated for the surface tension value was less than 0.05 mN m^{-1}.

Results and Discussion

It has been shown that the total molality of surfactants m and the composition of the second surfactant X_2 in the aqueous solution are the suitable thermodynamic independent variables to describe the adsorption behavior of surfactant mixture at constant temperature T and pressure p.[3,4] Here m and X_2 are defined as

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

and

$$X_2 = m_2/(m_1 + m_2), \tag{2}$$

where the subscripts 1 and 2 refer to 2-(octylsulfinyl)ethanol and decylammonium chloride, respectively. The surface tension γ of the aqueous solution of surfactant mixture was measured as a function of m at various X_2 values at 298.15 K under atmospheric pressure.

Figure 1(a) shows the plot of γ against m at constant X_2. It is seen that each curve has a break point at a relatively high surface tension and a relatively low concentration. It is also found that the m value of the break point increases, while the corresponding γ value decreases, as X_2 increases. The detailed features are given in Fig. 1(b), in which the γ *vs.* m curves are magnified around the break points. It has been already verified that the presence of a break point on the γ *vs.* m curve results from the phase transformation between two states in the adsorbed film.[1–4] Accordingly we can say that the phase transition takes place also in the present nonionic–ionic surfactant system. Taking up the γ values at a given m value from Figs. 1(a) and 1(b), the γ *vs.* X_2 curves are obtained as shown in Fig. 2. It is seen that γ increases with increasing X_2 and some curves have the break points connected by the dotted line. It is clear that the regions above and below the dotted line correspond to

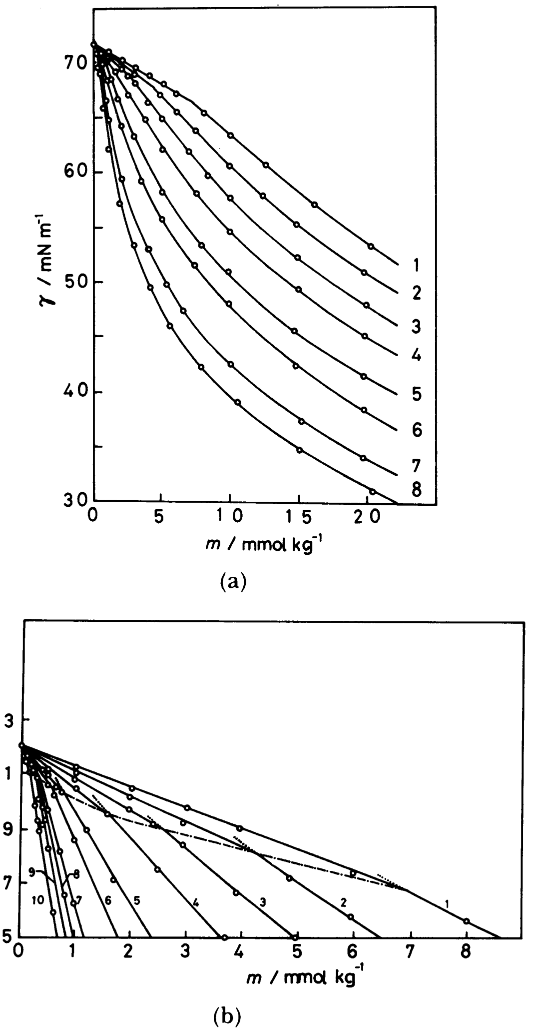

Fig. 1. (a) Surface tension *vs.* total molality curves at constant bulk composition: (1) $X_2=1$, (2) 0.979, (3) 0.950, (4) 0.901, (5) 0.801, (6) 0.700, (7) 0.360, (8) 0. (b) Surface tension *vs.* total molality curves at constant bulk composition: (1) $X_2=1$, (2) 0.979, (3) 0.950, (4) 0.901, (5) 0.801, (6) 0.700, (7) 0.496, (8) 0.360, (9) 0.200, (10) 0.

the different states in the adsorbed films. The surface tension of the phase transition point denoted by γ^{eq} is plotted against X_2 in Fig. 3. The value of γ^{eq} decreases slightly up to about 0.8 and then rapidly with increasing X_2. This behavior is undoubtedly related to the difference in the surface activity between the two surfactants as will be discussed later.

Now let us develop our thermodynamic treatment[3,4,12] so as to be applicable to the nonionic–cationic surfactant mixture. Since decylammonium chloride is a uni-uni valent strong electrolyte and 2-(octylsulfinyl)ethanol is a nonionic surfactant, the surface tension of the aqueous solution is expressed in the differential form as a function of the chemical potential of species at constant temperature and pressure:

$$d\gamma = -\Gamma_1^{\mathrm{H}} d\mu_1 - \Gamma_{2+}^{\mathrm{H}} d\mu_{2+} - \Gamma_{2-}^{\mathrm{H}} d\mu_{2-}, \qquad (3)$$

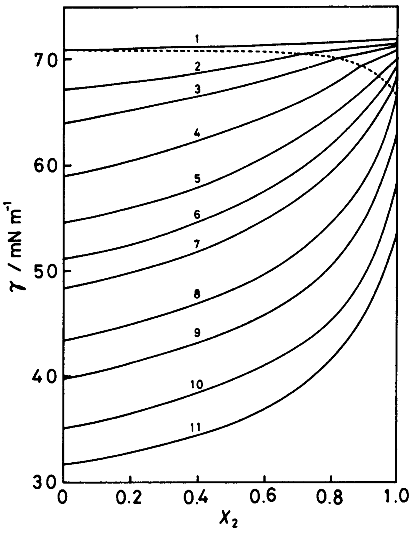

Fig. 2. Surface tension *vs.* bulk composition curves at constant total molality: (1) $m=0.2\,\mathrm{mmol\,kg^{-1}}$, (2) 0.5, (3) 0.8, (4) 1.5, (5) 2.5, (6) 3.5, (7) 4.6, (8) 7.25, (9) 10, (10) 15, (11) 20.

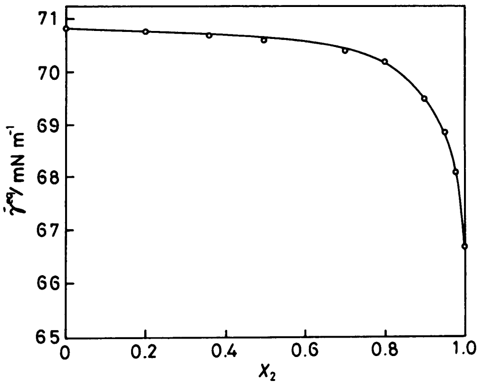

Fig. 3. Equilibrium surface tension *vs.* bulk composition curve.

where Γ_1^{H}, Γ_{2+}^{H}, and Γ_{2-}^{H} are the surface excess numbers of moles per unit surface area of 2-(octylsulfinyl)ethanol, decylammonium ion, and chloride ion, respectively. In Eq. 3, the surface excess quantities are defined with respect to the two dividing planes which make the surface excess numbers of moles of air and water be zero.[1,10] Taking notice that the suitable concentration variables are the total molality m and the composition X_2 defined by Eqs. 1 and 2 and assuming that the solution is ideal, Eq. 3 can be rewritten in the form

$$d\gamma = -RT[(\Gamma_1^{\mathrm{H}} + 2\Gamma_2^{\mathrm{H}})/m]dm - RT[(2X_1\Gamma_2^{\mathrm{H}} - X_2\Gamma_1^{\mathrm{H}})/X_1X_2]dX_2, \qquad (4)$$

where Γ_2^{H} is the surface excess number of moles of DeAC defined by

$$\Gamma_2^{\mathrm{H}} = \Gamma_{2+}^{\mathrm{H}} = \Gamma_{2-}^{\mathrm{H}}. \qquad (5)$$

By introducing the total surface excess numbers of moles of surfactants defined by

$$\Gamma^{H} = \Gamma_1^{H} + \Gamma_2^{H} \tag{6}$$

and the composition of DeAC in the adsorbed film by

$$X_2^{H} = \Gamma_2^{H}/\Gamma^{H}, \tag{7}$$

Eq. 4 is rearranged to yield

$$\mathrm{d}\gamma = -(RT\Gamma^{H}/m)(1+X_2^{H})\mathrm{d}m - (RT\Gamma^{H}/X_1X_2)[(2-X_2)X_2^{H} - X_2]\mathrm{d}X_2. \tag{8}$$

Thus we can evaluate the surface composition X_2^H by applying Eq. 8 to the experimental results:

$$X_2^{H} = [X_2 - (X_1X_2/m)(\partial m/\partial X_2)_{T,p,\gamma}]/[(2-X_2) + (X_1X_2/m)(\partial m/\partial X_2)_{T,p,\gamma}]. \tag{9}$$

The total surface density Γ^H, on the other hand, can be evaluated by

$$\Gamma^{H} = -[m/RT(1+X_2^{H})](\partial\gamma/\partial m)_{T,p,X_2}. \tag{10}$$

It should be noted that the value of Γ^H cannot be directly calculated from the derivative of γ with respect to *m* without knowing the values of X_2^H given by Eq. 9. This point is essentially different from the adsorption of ionic-ionic surfactant mixtures.

Let us first evaluate the composition of surfactants in the adsorbed film at constant *T, p,* and γ. Applying Eq. 9 to the *m vs.* X_2 curve shown by the full line in Fig. 4, which is obtained from Fig. 1(a), the value of X_2^H can be calculated numerically. The resulting *m vs.* X_2^H is depicted by the chain line in Fig. 4. Such a diagram gives us the relation between X_2^H and X_2 at a given value of γ. It is worth noting that the value of X_2^H is always smaller than the corresponding one of X_2. This implies that the difference in the surface activities between surfactants has a great influence on the surface composition. The diagrams 1 and 3, which are the ones for the gaseous and expanded films, respectively, have a shape essentially similar to each other, though the former is a deflated cigar type and the latter a swollen cigar one. When the phase transition takes place in the adsorbed film, the shape becomes more complicated as shown in Fig. 4 (diagram 2); the *m vs.* X_2 curve has a break point indicated by A and correspondingly the *m vs.* X_2^H curve changes discontinuously from the value of the gaseous film $X_2^{H,g}$ (point B) to that of the expanded film $X_2^{H,e}$ (point C). It is also seen that $X_2^{H,g}$ has a larger value than $X_2^{H,e}$, which is closely related to the variation of γ^{eq} with X_2 given in Fig. 3.[4] The present results are qualitatively akin to those of our previous ionic-ionic surfactant mixtures, but the diagrams are somewhat swollen compared with those of DAC-DeAC and DTAC-DeAC systems.[3,4] This suggests that OSE is more surface active than DTAC and DAC.

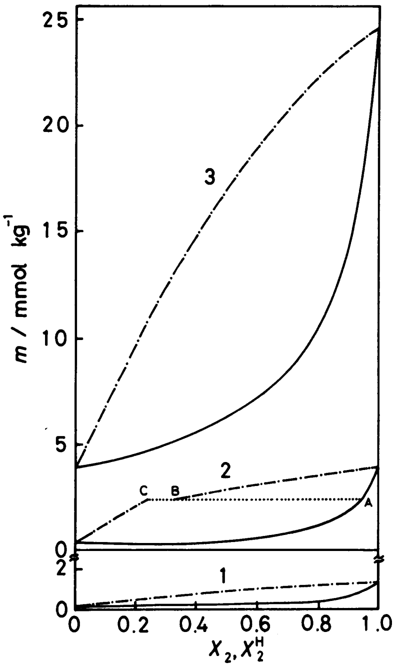

Fig. 4. Total molality *vs.* composition curves at constant surface tension: (1) γ=71 mN m^{-1}, (2) 69, (3) 50; (——) *m vs.* X_2, (-·-) *m vs.* X_2^H.

Now the values of Γ^H can be evaluated numerically by applying Eq. 10 to the experimental γ *vs. m* curves shown in Fig. 1(a) and using the X_2^H values calculated above. In Fig. 5 are drawn the Γ^H *vs. m* curves at various X_2 values. As is expected from Fig. 1, the value of Γ^H increases monotonously with *m* and changes discontinuously at the *m* value corresponding to the break point in Fig. 1. It is seen that the Γ^H value of OSE (X_2=0) is fairly large compared with that of DeAC (X_2=1). Taking account of the fact that the hydrocarbon chain length of OSE is shorter than that of DeAC, we can say that the repulsive force among the charged head groups of DeAC considerably diminishes its adsorption. Picking up the values of Γ^H at fixed *m* values in Fig. 5, the Γ^H *vs.* X_2 curves are depicted in Fig. 6. It is interesting to note that the variation of Γ^H with X_2 is considerably pronounced when X_2 is close to unity. Further, it is seen that the Γ^H value is nearly constant up to X_2=*ca.* 0.7 and then decreases suddenly with increase in X_2 at a high total concentration. This fact suggests that the OSE molecules play a predominant role in the adsorption behavior until the value of X_2 becomes considerably large because the surface activity of OSE is fairly high compared with that of DeAC.

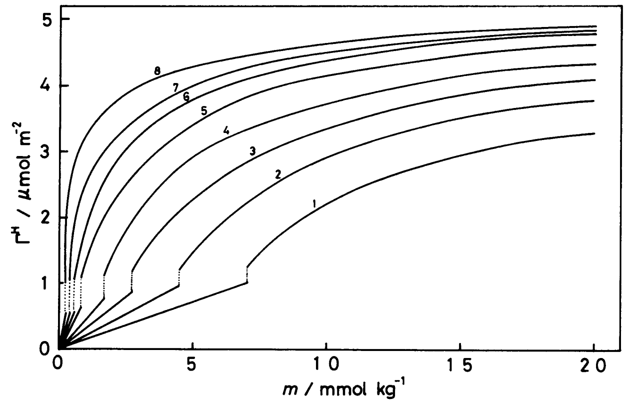

Fig. 5. Total surface density *vs.* total molality curves at constant bulk composition: (1) X_2=1, (2) 0.979, (3) 0.950, (4) 0.901, (5) 0.801, (6) 0.700, (7) 0.496, (8) 0.

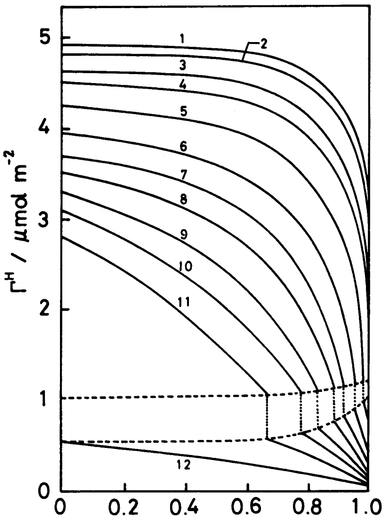

Fig. 6. Total surface density *vs.* bulk composition curves at constant total molality: (1) m=20 mmol kg^{-1}, (2) 15, (3) 10, (4) 8, (5) 5, (6) 3, (7) 2, (8) 1.5, (9) 1, (10) 0.75, (11) 0.5. (12) 0.2.

To make sure that the phase transition of the mixed adsorbed film takes place from a gaseous to an expanded state like those of pure OSE and DeAC films[2] and to get an insight into the film behavior, the surface pressure Π *vs.* the mean area per adsorbed molecule A curves are useful. Π and A are respectively defined by

$$\Pi = \gamma^0 - \gamma, \tag{11}$$

and

$$A = 1/N_{\mathrm{A}}\Gamma^{\mathrm{H}}, \tag{12}$$

where γ^0 is the surface tension of pure water and N_{A} is the Avogadro's number. By making use of Figs. 1 and 5, the Π *vs.* A curves at constant X_2 in Fig. 7 are obtained. It is seen that the shapes of the curves are similar to each other and vary regularly from the shape of OSE to that of DeAC. This proves that the phase transition of the mixed adsorbed films takes place from the gaseous to the expanded state.

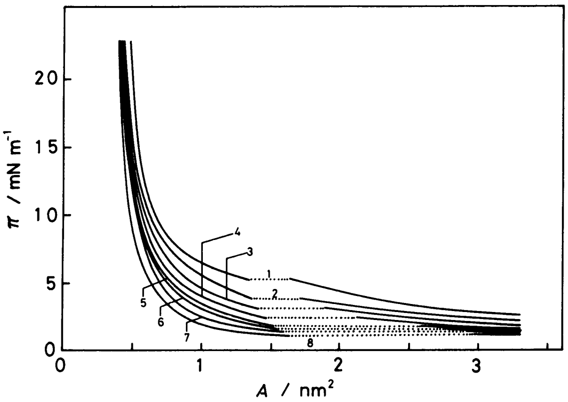

Fig. 7. Surface pressure *vs.* mean area per molecule curves at constant bulk composition: (1) X_2=1, (2) 0.979, (3) 0.950, (4) 0.901, (5) 0.801, (6) 0.700, (7) 0.496, (8) 0.

For mixed insoluble films spread on water, the Π *vs.* A curves are depicted under the condition that the film composition is kept constant. For mixed adsorbed films, the corresponding curves can be drawn; the results are shown in Fig. 8. Comparing Fig. 8 with Fig. 7, we notice that the dependence of the isotherm on the composition is more regular when X_2^{H} is kept constant. Further it is important to note that the equilibrium transition pressure γ^{eq} between the gaseous and expanded films increases with decreasing A in Fig. 8 while it is constant in Fig. 7.

We have previously shown[3,4] that the phase transition between the gaseous and expanded states of the mixed adsorbed film can be well described by the plots of γ^{eq} against the compositions of the gaseous film $X_2^{\mathrm{H,g}}$ and the expanded film $X_2^{\mathrm{H,e}}$ corresponding to the two-dimensional phase diagram used commonly in the study of mixed insoluble monolayers.[13] The numerical values of $X_2^{\mathrm{H,g}}$ and $X_2^{\mathrm{H,e}}$ can be obtained from the diagram 2 in Fig. 4 and the analogous ones at other γ^{eq} values; the phase diagram is illustrated in Fig. 9. The areas above the γ^{eq} *vs.* $X_2^{\mathrm{H,g}}$ curve and below the γ^{eq} *vs.* $X_2^{\mathrm{H,e}}$ curve correspond to the region of the gaseous and the expanded phase, respectively. It turns out that the value of $X_2^{\mathrm{H,e}}$ is smaller than that of $X_2^{\mathrm{H,g}}$ over the whole range. This observation is the same as that obtained for the ionic–ionic surfactant

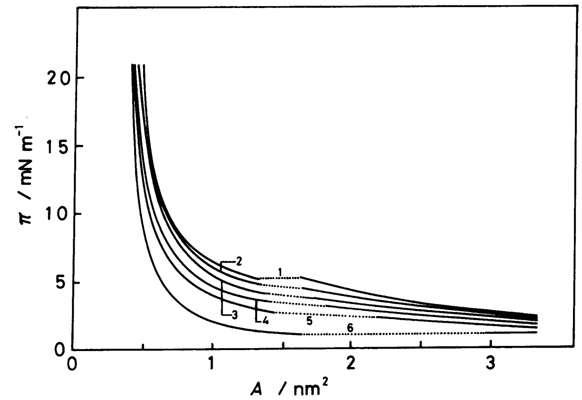

Fig. 8. Surface pressure *vs.* mean area per molecule curves at constant surface composition: (1) X_2^{H}=1, (2) 0.8, (3) 0.6, (4) 0.4, (5) 0.2, (6) 0.

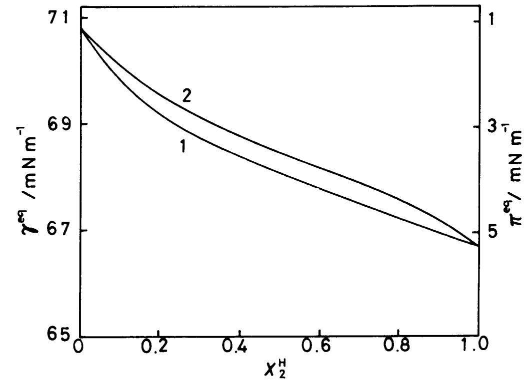

Fig. 9. Equilibrium surface tension (pressure) *vs.* surface composition curves: (1) $\gamma^{\mathrm{eq}}(\Pi^{\mathrm{eq}})$ *vs.* $X_2^{\mathrm{H,e}}$, (2) $\gamma^{\mathrm{eq}}(\Pi^{\mathrm{eq}})$ *vs.* $X_2^{\mathrm{H,g}}$.

mixtures in our previous papers.[3,4] The phase diagrams, however, are different in shape; the present one has a cigar form and the previous ones have crescent shaped forms. This fact indicates that the difference in the surface activity between two surfactants of the present system is larger than DAC–DeAC and DTAC–DeAC systems.

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