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Surface Activity of Complex in Mixed Surfactant Solution

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The dissociation constant of the complex formed in the mixed and very dilute surfactant solution of 3-(dodecylammonio)-propionate (NDA) and sodium alkylsulfates (C_{10}, C_{12}, C_{14}) (SAS) was determined by measuring surface tension and adsorbed amounts of the solution. The composition in the surface and bulk phases did not coincide at the equimolar mixture. The adsorbed monolayer on the solution consists of the coadsorption of NDA–SAS complex (1:1) and free NDA, while the adsorption of free SAS was almost zero in various concentrations studied. Under these conditions the surface activity of the complex alone was obtained. The relationship between the surface activity and bulk concentration for each mixed solution was discussed in terms of relative adsorbability. The surface activity of the complex was one order of magnitude higher than that of NDA and two orders higher than that of SAS.

The mixed surfactant in the aqueous solution has been found to have a more surface-active character than that of each component:[1–10] in particular, the solution containing oppositely charged surfactants considerably changes by the formation of an ionic complex. There are a few papers which have described the dissociation constant of a surfactant complex, which is formed in a solution.[7,11,12] Corkill *et al.*,[2,3] who studied the solution of mixed surfactant of sodium alkyl sulfates and hexadecyltrimethylammonium bromide (HTAB), found that an adsorbed layer composed of the equimolar complex of these surfactants was independent of the bulk compositions, but that the complex formation did not take place in the bulk phase.

The surface activity of a surfactant solution is remarkably enhanced even in dilute solution when a complex is formed, but the concentration of each single species decreases only slightly. Thus a direct measurement of concentration reliable enough for determining the dissociation constant is impossible in some cases. In view of such properties of surfactant solutions, the present work was carried out to determine the dissociation constant of a surfactant complex in a mixed and very dilute solution by the surface chemical method, and to decide the surface activity due to the complex in the solution. Further, an attempt was made to elucidate the relationship between the surface activity and the bulk compositions in the solution.

Experimental

The pure and synthetic surfactants 3-(dodecylammonio)-propionate (NDA) and sodium alkyl sulfates (SAS) containing 10 (De), 12 (D), and 14 (T) carbon atoms were used. Surface tension and adsorbed amounts were measured by the Wilhelmy and the radiotracer methods, respectively. In radiometry, NDA was labelled with tritium and SAS with ^{35}S, respectively. The details of these measurements were described in previous papers.[13–15] The temperature was maintained at 30.0±0.2 °C, and the pH of the solutions was 5.8±0.2. A part of the data obtained in the present studies has been reported elsewhere.[16,17]

Results and Discussion

The complex formation in the mixed solution of NDA and SAS was confirmed by the electrophoresis study using radioactive surfactants.[17] The conductivity measurements for the solution, however, did not show any indication of complex formation in the solution, as had been found in the mixed SAS–HTAB solution,[3] probably because the concentration of complex is too low for the detection method.

In order to study the composition of the complex of NDA and SAS (*e.g.* SDS), the surface tension was measured for the single and mixed solutions of NDA and SDS. The results are shown in Fig. 1. The dotted line in the figure represents the difference in the surface tensions between the mixed and the (ideal) hypothetical mixed solutions of NDA and SDS. The maximum deviation occurred at the equimolar composition of the mixed solution. This fact leads to the conclusion that the NDA–SDS complex in the bulk phase has a stoichiometric composition in 1:1 molar ratio. This coincided with the results of elemental analysis on the precipitate which was prepared by mixing the NDA and SDS solutions at high concentrations.[17]

Determination of the Dissociation Constant of Complex. A complex, if it is surface-active, always coadsorbs at its solution surface, independently of the surface behaviors of the other species in the solution. Hence, the Gibbs adsorption isotherm may be applied to such a surface-active solution.[18] In present adsorption system, the solute species in the solution are limited

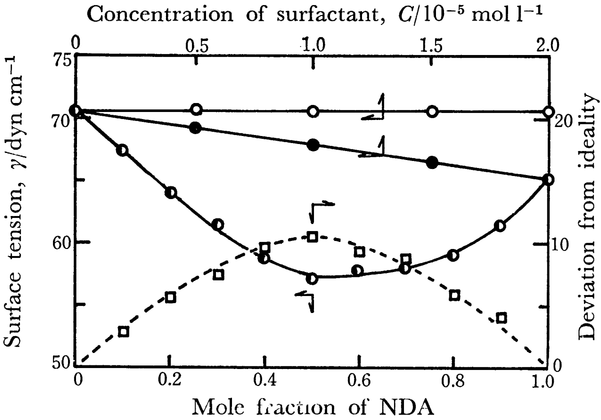

Fig. 1. Surface tension *vs.* concentration curves for the solutions of NDA(●), SDS(○) and their toatal constant mixture (◐). A dotted line shows the difference of surface pressures in the ideal and real mixed solutions,

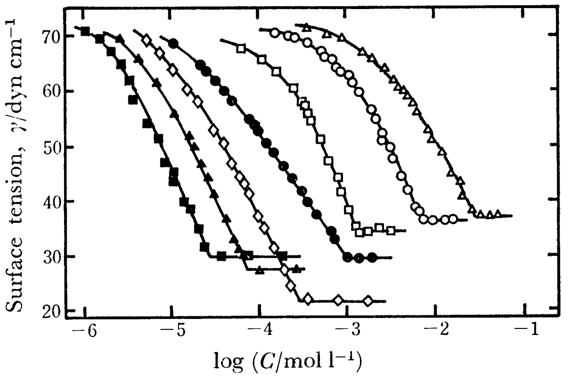

Fig. 2. Surface tension *vs.* logarithmic concentration curves for the solutions of SDeS(△), SDS(○), STS (□), NDA(●) and the equimolar mixed solutions of NDA-SDeS(◇), NDA-SDS(▲), and NDA-STS (■).

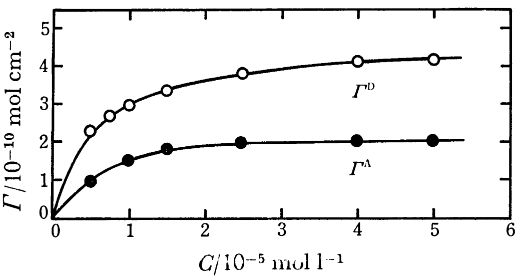

Fig. 3. Adsorption isotherms of equimolar mixed solutions. Γ^D was measured on the ^{3}HNDA-SDS solution, Γ^A on NDA-^{35}SDS.

to sodium (Na), alkyl sulfate (A), ampholyte (D), and complex (C) ions, and these are related to:

$$A^- + D^\pm \underset{K}{\rightleftharpoons} C^-$$

Previous observations[15,19] showed that the hydrolyses of the surfactants did not have to be considered under the present experimental conditions. Since the activity coefficients of these ions may be put at unity due to the low concentration, the dissociation constant of the complex, *K*, in the bulk phase can be defined in terms of the surface-chemical parameters as follows (see Appendix):

$$K = \frac{1}{4C}\left[\left(\frac{\Gamma^D+\Gamma^A}{2I-3\Gamma^D-\Gamma^A}\right)^2-1\right] \qquad (1)$$

where

$$\left.\begin{aligned} I &= -(d\gamma/RT d\ln C)_{1:1}, \\ C &= C_A + C_C = C_D + C_C = C_{Na}, \\ \Gamma^D &= \Gamma_D + \Gamma_C, \\ \text{and} \quad & \\ \Gamma^A &= \Gamma_A + \Gamma_C = \Gamma_{Na}. \end{aligned}\right\} \qquad (2)$$

C is the concentration in the apparent equimolar mixed solution of NDA and SAS, γ the surface tension, Γ the surface excess, *R* the gas constant, and *T* the absolute temperature. The subscripts and superscripts mean the effective and apparent quantities for each species, respectively. *K* in Eq. 1 may be estimated, if the surface tension and the adsorbed amounts are measured as a function of the concentration *C*. Figure 2 shows the γ *vs.* logarithmic concentration plot for the NDA and SAS solutions. Γ^D and Γ^A measured by radiometry are shown in Fig. 3. Similar tendencies were observed for the NDA-SDeS and NDA-STS solutions. The *K* values obtained are listed in Table 1. The effective concentrations, then, can be estimated for each species in the mixed surfactant solutions of NDA and SAS by using the *K* values.

TABLE 1. DISSOCIATION CONSTANT FOR NDA-SAS COMPLEXES IN AQUEOUS SOLUTION (30 °C)

Complex	*K* l/mol × 10^{-4}
NDA-SDeS	1.32
NDA-SDS	6.54
NDA-STS	33.6

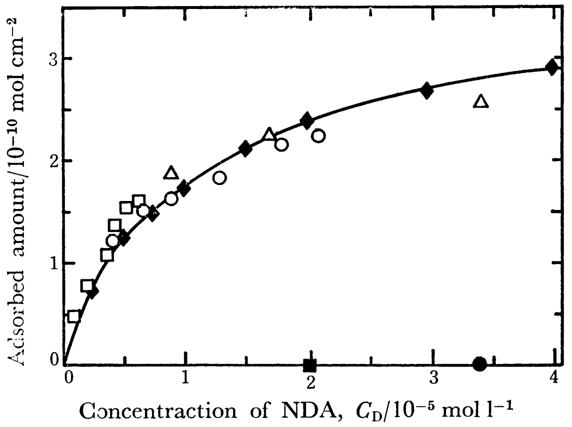

Fig. 4. Comparison of the $\Delta\Gamma$ values for each mixture with the adsorption isotherm of single NDA solution (◆). △: NDA-SDeS, ○: NDA-SDS, □: NDA-STS. Adsorbed amounts of the single SDS(●) and STS(■) solutions are plotted at the same concentration scale with NDA solution.

Surface Composition. As shown in Fig. 3, the adsorption isotherms, Γ^D and Γ^A, which were independently measured with respect to each radioactive solution of ^{3}H labelled NDA-SAS and NDA-^{35}S labelled SAS at the same concentration *C*, did not coincide with each other even at the equimolar mixed solution. To study this difference, the surface activity was examined for each single solution of NDA and SAS at the concentrations corresponding to those which were estimated for each NDA-SAS solution by the *K* values. Neither surface excess nor surface tension lowering was observed for the SAS solutions, within the experimental error (see Fig. 4).[14,15,20] Then, it may be fairly asserted that Γ_A is zero at various concentrations under consideration. Since Γ_A was zero, the difference, $\Delta\Gamma$, of the Γ^D and Γ^A isotherms in Fig. 3 was compared with the surface excess, Γ_D^0, measured at the same effective concentration of the single NDA solution. The results are shown in Fig. 4. The $\Delta\Gamma$ values obtained for all NDA-SAS systems are in fairly good coincidence with the Γ_D^0 values. Then $\Gamma_A \simeq 0$ and $\Delta\Gamma \simeq \Gamma_D^0$; therefore, Γ^A is Γ_C. Consequently, the difference of isotherms in Fig. 3 can be explained by

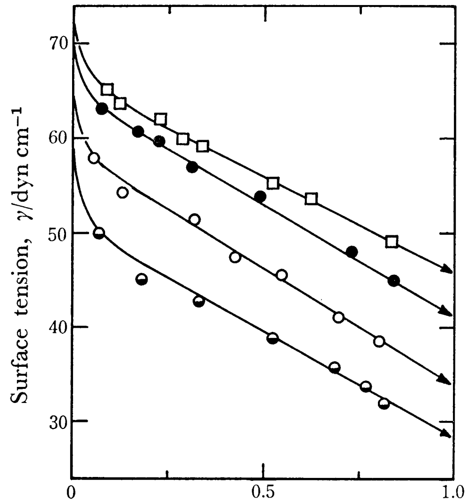

Fig. 5. Dependence of surface tension on complex concentration. Concentration of NDA ($M\times10^5$) was kept at 0.60(□), 1.00(●), 2.00(○) and 3.60(◒). Arrows show the surface tension of complex alone.

the facts that the adsorbed monolayer from the mixed solution consists of the coadsorption of the complex of NDA–SDS and NDA, while the adsorption of SDS owing to the single dispersion in the solution is almost zero, as shown experimentally for SDS and STS in Fig. 4.

Surface Activity of Complex. Attempts were made to determine the surface activity of the complex alone, though direct measurements are of course impossible. The dependence of surface tension on composition of the film which consists of several species has not been elucidate for the adsorbed monolayer. However, the following linear relation is frequently found, in the bulk ternary system, between its surface tension and the mole fraction of solutes (1,2) at constant amount of solvent:[21]

$$\gamma = X_1\gamma_1 + X_2\gamma_2 \tag{3}$$

If γ is measured as a function of mole fraction, the extrapolated surface tensions for each single solution can be obtained at various concentrations:

$$\gamma_2^0 = (\lim_{X_2\to1}\gamma)_C$$

By this manner the surface tension of a complex may be obtained. The complex solutions for this purpose were prepared at various concentrations by adding varying amounts of SAS to the NDA solution of the constant concentration. The fraction of complex formation, X_C, in the solution was calculated from $X_C=C_C/C^D$ by using the K values shown in Table 1. Figure 5 is the plot of surface tension against X_c. Though the present solution contains four species, the apparent additivity expressed by Eq. 3 was well established in a wide region of mole fraction for the complex.[22] The surface tension obtained by extrapolating X_C to 1, corresponding to that for the solution of complex alone, is shown in Fig. 6 as a function of complex concentration, C_C, though only two points were obtained for SDeS and STS complexes. The surface excess, Γ_C^0, of complex was calculated from Fig. 6 by Eq. 4, assuming an ideal solution for the complex:

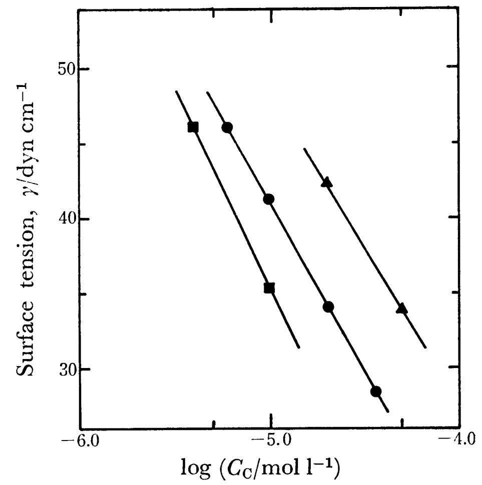

Fig. 6. Surface tension *vs.* concentration curves for the complex solutions. ▲: NDA–SDeS, ●: NDA–SDS, ■: NDA–STS.

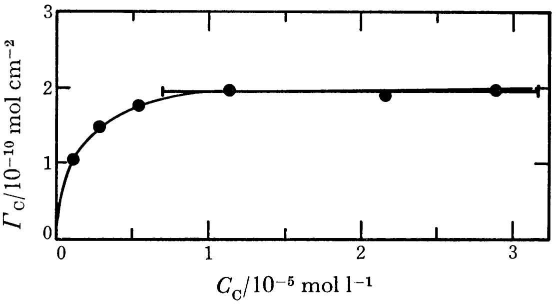

Fig. 7. Adsorption isotherm of NDA–SDS complex. Heavy solid line is the Γ_C^0 values calculated from Eq. 4.

$$\Gamma_C^0 = -\frac{1}{2RT}\left(\frac{\partial\gamma}{\partial\ln C_C}\right)_{NDA} \tag{4}$$

On the other hand, the Γ^A isotherm in Fig. 3 is seen to be the Γ_C isotherm, according to the argument in the previous section. The Γ_C^0 values calculated from Eq. 4 are compared with the "observed" isotherm for the NDA–SDS complex in Fig. 7. Both curves were in good agreement for either the NDA–SDeS or the NDA–STS complex. This is an experimental approval for the present approach.

In order to compare the surface activity of a complex to that of NDA, the relative adsorbability, α, was obtained by means of Eq. 5, which was defined so as to eliminate the concentration dependence near the close-packing adsorption:

$$\alpha = \lim_{C_1\to0}\frac{\Gamma_1}{C_1}\Big/\lim_{C_D\to0}\frac{\Gamma_D}{C_D} \tag{5}$$

The results are shown in Table 2. It was found that the surface activity of complex is larger by one order of magnitude than that of NDA and also larger by two orders of magnitude than that of SAS. The increment of chain-length of alkyl sulfates incorporated in the complex is likely to enhance exponentially the surface activity of complex, as in free SAS. It is of interest that the increasing rate of α values for a series

TABLE 2. RELATIVE ADSORBABILITY OF COMPLEX AND SAS TO NDA

Surfactant	$\lim_{C\to 0}(\Gamma/C)$, 1/cm$^2\times 10^{-5}$	α
NDA	0.313	1
SDcS	0.028	0.089
SDS	0.041	0.13
STS	0.059	0.19
NDA-SDeS	5.02	16.0
NDA-SDS	10.3	32.9
NDA-STS	20.5	65.5

of free SAS is rather less than that in the state complexed with NDA. This tendency might be reasonable, because the initial inclination in the isotherm is expected to increase more or less exponentially with increasing chain-length of surfactant.[14,23,24]

The present method will be applicable in general to the determination of the dissociation constant of a complex which is formed either by the chelation or by the association reaction, if at least one of the species in the solution is surface-active.

Appendix

The Gibbs adsorption isotherm is written for the present system as follows:

$$-\frac{\mathrm{d}\gamma}{RT} = \Gamma_{\mathrm{A}}\mathrm{dln}C_{\mathrm{A}} + \Gamma_{\mathrm{D}}\mathrm{dln}C_{\mathrm{D}} + \Gamma_{\mathrm{Na}}\mathrm{dln}C_{\mathrm{Na}} + \Gamma_{\mathrm{C}}\mathrm{dln}C_{\mathrm{C}} \tag{A1}$$

In the equimolar mixed solution, when a complex is formed at 1 : 1 molar ratio, K is written

$$K = \frac{C_{\mathrm{C}}}{C_{\mathrm{A}}\cdot C_{\mathrm{D}}} = \frac{C_{\mathrm{C}}}{C'^2} \tag{A2}$$

where, $C'=C_{\mathrm{A}}=C_{\mathrm{D}}>0$. Substituting Eqs. 2 and A2 into Eq. A1, we have

$$I = (\Gamma^{\mathrm{A}}+\Gamma^{\mathrm{D}})\frac{2KC}{1+4KC-(1+4KC)^{1/2}} + \Gamma^{\mathrm{A}} \tag{A3}$$

By introducing the substitution $(1+4KC)^{1/2}=A$, $(A\neq 1)$, we have

$$A = \frac{\Gamma^{\mathrm{A}}+\Gamma^{\mathrm{D}}}{2I-3\Gamma^{\mathrm{A}}-\Gamma^{\mathrm{D}}} \tag{A4}$$

Then, we may obtain Eq. 1.

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22) Attention should be paid to the fact that the contribution of single dispersed SAS to the surface tension lowering is completely negligible in the region of these concentrations (see Fig. 2).

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24) The initial inclination of the isotherm is approximately related to the number of carbon atoms, N, in a surfactant as follows: $\lim_{C\to 0}\Gamma/C \propto N\exp N$.