The Adsorption of the Ampholytic Surfactant and the Anionic Surfactant at the Nitrogen–Solution Interface from the Mixed Aqueous Solution

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The amounts of adsorption of an ampholytic surfactant, *N*-dodecyl-*β*-alanine(NDA), and an anionic surfactant, sodium alkylsulfate(SAS), at nitrogen–solution interface from aqueous equimolar mixtures of them were measured directly by the radiotracer method, using tritiated and non-tritiated samples of NDA and ^{35}S-labeled and non-labeled samples of SAS: sodium tetradecylsulfate(STS), sodium dodecylsulfate(SDS), and sodium decylsulfate(SDeS). The adsorption of both components of the mixed systems was observed at concentrations lower than those for the systems containing each component alone. A stronger adsorption of NDA than that of SAS was observed for all mixed systems. The overall area per alkyl chain at the maximum adsorption was about 26 Å^2 for each system, showing the adsorbed layer to be in a highly condensed state. Electrophoresis measurements, together with surface tension measurements of NDA–SDS systems and the elemental analysis of the precipitates from concentrated NDA–SDS solutions, suggested the presence of a 1 : 1-complex formed between NDA and SDS. The Gibbs adsorption isotherm for the binary system was derived. The calculated amounts of adsorption agreed with the observed values. A linear relationship was found to hold between the logarithm of the constants of complex formation and the number of carbon atoms of SAS. A free energy of the complex formation of −0.50 kcal per mole of the methylene group was found.

A number of studies have been made of the interaction between organic cations and anions in solutions, such as surfactant–surfactant[1–6] and surfactant–dye[7–11] systems, where the formation of ion pairs or association complexes may occur. Especially in an aqueous solution containing anionic and cationic surfactants, surface tension depression and micelle formation[1,6] have been observed at lower concentrations than in single-surfactant solutions, suggesting the formation of a complex with high surface activity and a mixed micelle.

Similar effects can be expected to occur in an aqueous mixture of ampholytic and ionic surfactants. However, studies of such mixtures are rather rare.[12] In the present study, the measurements of the adsorption of the ampholytic surfactant, *N*-dodecyl-*β*-ananine (NDA), and anionic surfactants including sodium tetradecylsulfate(STS), sodium dodecylsulfate(SDS), and sodium decylsulfate(SDeS) from equimolar aqueous solutions of them were made by the radiotracer method, together with measurements of the surface tension of these systems. The Gibbs adsorption isotherm for an aqueous system containing two surfactants and an equimolar complex was derived and was confirmed to be applicable to the system. The formation of a complex between two solute species was inferred, and the equilibrium constants of complex formation and the free energy of complex formation per methylene group of surfactants were estimated.

Experimental

Materials. Tritiated NDA was synthesized from tritiated dodecylamine and *β*-propiolactone and was purified as has been reported.[13] The specific activity of the sample was about 16 Ci/mol. ^{35}S-labeled sodium alkylsulfate, STS, SDS, and SDeS were synthesized by allowing them to react the corresponding alcohols with ^{35}S-labeled sulfuric acid, were purified by repeated recrystallization from ethanol, and were dried *in vacuo*. The specific activity of the samples was about 1 Ci/mol. The water used was prepared by refluxing ordinary distilled water with acid permanganate, then by distilling it from an alkaline permanganate solution, and finally by distilling twice using a Hysil flask.

Methods. The radiotracer method of adsorption measurement was similar to that reported previously.[14] Two solutions of the same composition were prepared, one containing ^{3}H-NDA and SAS, and the other, ^{35}S-SAS and NDA, in order to measure the amounts of the adsorption of both components for a given solution separately. The surface tension was measured by the Wilhelmy plate method. The time dependence of the surface tension was self-recorded, and the curve was extrapolated to an infinite time in order to obtain an equilibrium value. All the measurements were made at 30 °C in the neutral pH region, where NDA molecules have been confirmed to be in the zwitterionic state.[15]

Results and Discussion

Surface Tension. Figure 1 shows the surface tension *vs.* concentration curves of NDA and equimolar mixtures of NDA and SAS's of 4 to 14 carbon

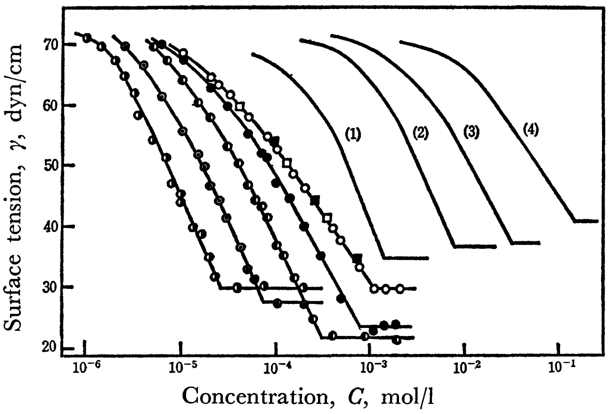

Fig. 1. Surface tension *vs.* concentration of NDA–SAS, NDA and SAS solutions.
○: NDA solution
mixed solution of NDA and
◑: STS, ⊙: SDS, ◐: SDeS, ●: sodium octylsulfate
□: sodium hexylsulfate, ■: sodium butylsulfate
SAS solution: (1) STS, (2) SDS, (3) SDeS, (4) sodium octylsulfate

atoms in a molecule. The abscissa shows the concentration of each component of the mixed solutions. The surface tension of SAS is also shown for the sake of comparison.[16] It is noticeable that DNA shows a lower critical micelle concentration and a smaller slope than those of SAS. The surface tension of NDA–SAS mixtures in an equimolar ratio is generally far lower than that expected from the surface tensions of solutions containing each component alone.

Thus, a synergistic effect of surface activity was confirmed. The effect increases with the increase in the surface activity of SAS's. This suggests some kind of interaction between NDA and SAS's, depending on the hydrocarbon chain length of the latter.

Adsorption. Figures 2, 3, and 4 show the observed amounts of the adsorption of both NDA and SAS from their equimolar mixtures for the systems of NDA–STS, NDA–SDS, and NDA–SDeS respectively. The amount of adsorption is larger for NDA than for SAS, and the amounts of the adsorption of NDA and SAS increase at a nearly constant ratio with the increase in the concentration, tending toward saturation. The amount and the molar fraction of the adsorption of SAS in the mixed systems increase with the increase in their alkyl chain length.

The adsorbed layers observed in the present study show an overall area of about 26 Å^2 per molecule and are highly condensed compared with those of each of the components, which show the values of 43 Å^2 per molecule for NDA[13] and 52 Å^2 for SDS[14] at their saturated adsorption. The value of 26 Å^2 is even smaller than that of the mixed solution containing anionic and cationic surfactants, *i.e.*, 30 Å^2.[4] These facts also suggest the interaction of NDA with SAS in the adsorbed layer.

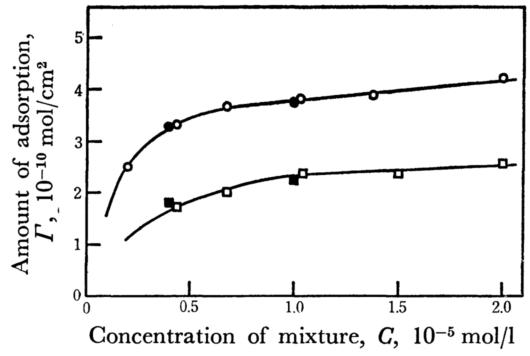

Fig. 2. Amount of adsorption of NDA and STS.
Observed value ○: NDA, □: STS
Calculated value ●: NDA, ■: STS

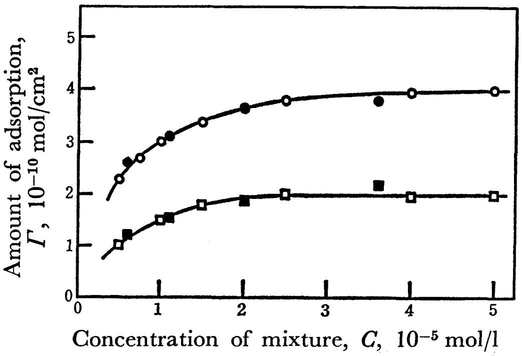

Fig. 3. Amount of adsorption of NDA and SDS.
Observed value ○: NDA, □: SDS
Calculated value ●: NDA, ■: SDS

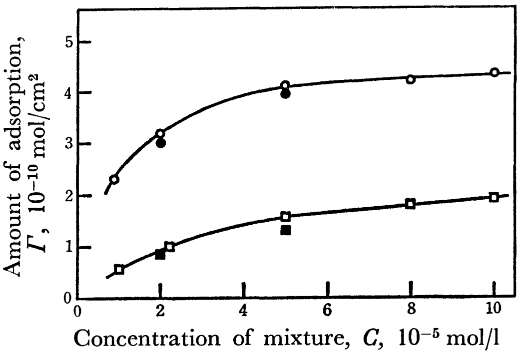

Fig. 4. Amount of adsorption of NDA and SDeS.
Observed value ○: NDA, □: SDeS
Calculated value ●: NDA, ■: SDeS

As regards the interactions between oppositely charged organic ions in a bulk solution, the formation of a complex with a 1 : 1-molar ratio has been reported for surfactant–surfactant and surfactant–dye systems by many investigators on the basis of studies of conductometry,[2,8,9] spectrophotometry,[3,11] the elemental analysis of precipitates,[3,5,8] and polarography.[10] Similar interactions of NDA with SDS in an acid solution, and with dodecyltrimethylammonium bromide in an alkaline solution, have been investigated.[12] However, the interaction between an anionic surfactant such as SAS and the zwitterionic NDA in the near neutral pH region[15] has not yet been experimentally confirmed.

In order to confirm whether or not a 1 : 1-complex forms in the present case, the electrophoresis of NDA in an aqueous SDS solution, elemental analysis of the precipitates obtained from NDA–SDS mixtures were carried out. A surface tension *vs.* composition curve was also constructed in order to examine the complex formation.

Electrophoresis. As is shown in Fig. 5, a U-tube 0.7 cm in diameter and 30 cm in length, with an opening with a rubber stopper 10 cm from a porous plate at the bottom, was used for this purpose. Platinum electrodes were put in both arms of the tube. An equimolar solution of 4×10^{-5} mol/l ^{3}H-NDA and

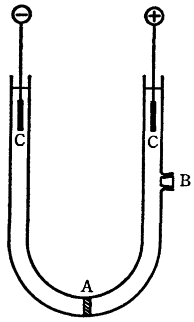

Fig. 5. Apparatus for electrophoresis.
A: porous plate, B: small opening with rubber stopper, C: platinum electrodes

SDS was introduced into the left arm while the same solution without radioactivity was introduced in the right arm. Then, a 200-volt DC current was applied between the electrodes about 30 cm apart through the solution; the migration of ^{3}H-NDA into the right arm was detected by measuring the radioactivity of a sample of about 1 μl of the solution taken out by means of a microsyringe through the rubber stopper. When the left electrode was made negative as shown, the radioactivity began to be detected several minutes after applying the DC voltage. In the absence of SDS, the migration of NDA was not detected even after a prolonged time. This indicates no net charge in the NDA, that is, the zwitterionic state of NDA in the solution without SDS and the net negative charge of NDA in the mixed solution, which would be evidence of NDA–SDS complex formation. Here, the size of the complex formed may not be so large as an ordinary micelle, since the concentration is sufficiently below the break-point of the surface tension *vs.* concentration curve shown in Fig. 1.

Elemental Analysis. When NDA and SDS solutions of concentrations sufficiently higher than that used for surface tension measurements were mixed at about 20 °C, a white precipitate appeared. The results of the elemental analysis of the precipitates are shown in Table 1. The molar ratio of NDA to SDS was conventionally estimated from the nitrogen-to-carbon ratio as shown in the last column. The values are found to be nearly unity for the wide range of SDS : NDA molar ratios of the solutions studied. Thus, the 1 : 1-complex formation can be confirmed, at least in the state of the precipitate, suggesting that 1 : 1-complex ions may also exist in the solution.

Surface Activity. Figure 6 shows the surface tension plotted against the molar ratio of NDA to SDS plus NDA in the solution with the total concentration kept constant at 2×10^{-5} mol/l (Curve 1), together with its deviation from the surface tension calculated assuming the additivity of the surface tension depression for each component (Curve 2). Curve 2 exhibits a distinct maximum at the molar ratio of 1 : 1. Again, this suggests a complex formation in the aqueous solution between NDA and SDS at this ratio.

Table 1. Elemental analysis of precipitates from NDA-SDS solutions

Composition of solution		Composition of precipitate		Molar ratio of precipitate
SDS	NDA	nitrogen	carbon	NDA/SDS
1 mM	1 mM	2.50%	54.12%	1.068
2	1	2.10	53.13	0.914
10	1	2.40	52.02	1.067

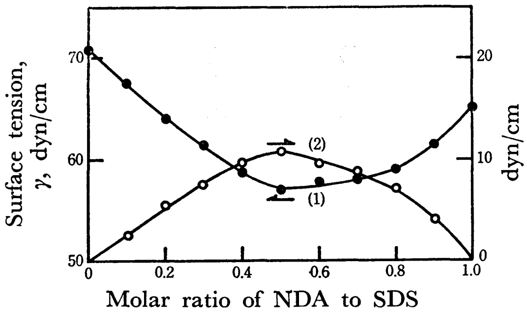

Fig. 6. Surface tension of NDA-SDS system.
(1) Surface tension of NDA-SDS system, total concentration; 2×10^{-5} mol/l.
(2) Deviation of surface tension from the additivity (see text).

The Gibbs Adsorption Isotherm for the Binary System of the Surfactants. The Gibbs adsorption isotherm giving the amount of each component adsorbed from the mixed aqueous solution of ampholytic and anionic surfactants was derived. The Gibbs adsorption isotherm is written, in its general form, as:[17)]

$$-\mathrm{d}\gamma/RT = \sum_i \Gamma_i \,\mathrm{d}\ln a_i \tag{1}$$

where γ denotes the surface tension, and Γ_i and a_i, the surface excess and the activity of the i'th solute in the solution respectively. Equation (1) is rewritten for a solution containing the ampholytic (NDA) and the anionic (SAS) surfactants as:

$$\begin{aligned}-\mathrm{d}\gamma/RT &= \Gamma_\mathrm{D}\,\mathrm{d}\ln C_\mathrm{D} + \Gamma_\mathrm{Na}\,\mathrm{d}\ln C_\mathrm{Na}\\ &\quad + \Gamma_\mathrm{A}\,\mathrm{d}\ln C_\mathrm{A} + \Gamma_\mathrm{C}\,\mathrm{d}\ln C_\mathrm{c}\end{aligned} \tag{2}$$

where the activities are replaced by concentrations, since the concentration of the surfactants used is of the order of magnitude of 10^{-5} mol/l; subscripts D, Na, A, and C refer to the alkylsulfate, the sodium, the ampholyte, and the complex ions respectively. Here, as has been mentioned above, we have sufficient reason to assume the 1 : 1-complex formation between NDA and SAS. Therefore, the following equation can be expected to hold:

$$C_\mathrm{C}/C_\mathrm{A}C_\mathrm{D} = K \tag{3}$$

where K is the equilibrium constant of the complex formation. We also obtain the following equation from the condition of electrical neutrality in the adsorbed phase:

$$\Gamma_\mathrm{Na} = \Gamma^\mathrm{D} \tag{4}$$

From Eqs. (2), (3), and (4), we obtain:

$$-\mathrm{d}\gamma/RT = \Gamma^\mathrm{D}(\mathrm{d}\ln C_\mathrm{D} + \mathrm{d}\ln C_\mathrm{Na}) + \Gamma^\mathrm{A}\,\mathrm{d}\ln C_\mathrm{A} \tag{5}$$

where $\Gamma^\mathrm{A} = \Gamma_\mathrm{A} + \Gamma_\mathrm{C}$ and $\Gamma^\mathrm{D} = \Gamma_\mathrm{D} + \Gamma_\mathrm{C}$ are the total amounts of the adsorption of NDA and SAS respectively. In order to obtain Γ^D and Γ^A, we should derive two equations from Eq. (5). For this purpose, Eq. (5) is differentiated under two appropriate conditions. First, we differentiate Eq. (5) with respect to the logarithm of the equimolar concentration, keeping the molar ratio of NDA to SAS constant at unity:

$$\begin{aligned}-[\mathrm{d}\gamma/RT\,\mathrm{d}\ln C]_{1:1} &= \Gamma^\mathrm{D}[(\mathrm{d}\ln C_\mathrm{D}/\mathrm{d}\ln C)_{1:1}\\ &\quad + (\mathrm{d}\ln C_\mathrm{Na}/\mathrm{d}\ln C)_{1:1}]\\ &\quad + \Gamma^\mathrm{A}(\mathrm{d}\ln C_\mathrm{A}/\mathrm{d}\ln C)_{1:1}\end{aligned} \tag{6}$$

where C denotes the concentration of the equimolar mixture given by:

$$C = C_\mathrm{A} + C_\mathrm{C} = C_\mathrm{D} + C_\mathrm{C} = C_\mathrm{Na} \tag{7}$$

From Eqs. (3) and (7), we obtain, for the equimolar mixture:

$$
\begin{aligned}
(\mathrm{d}\ln C_{\mathrm{D}}/\mathrm{d}\ln C)_{1:1} &= (\mathrm{d}\ln C_{\mathrm{A}}/\mathrm{d}\ln C)_{1:1} \\
&= (C/C_{\mathrm{A}})(\mathrm{d}C_{\mathrm{A}}/\mathrm{d}C)_{1:1} \\
&= 2KC/(1+4KC-\sqrt{1+4KC}) \qquad (8)
\end{aligned}
$$

From Eqs. (6), (7) and (8), we obtain:

$$I_{1:1} = (p+1)\Gamma^{\mathrm{D}} + p\Gamma^{\mathrm{A}} \qquad (9)$$

where:

$$I_{1:1} = -(\mathrm{d}\gamma/RT\,\mathrm{d}\ln C)_{1:1}$$

$$p = 2KC/(1+4KC-\sqrt{1+4KC})$$

Next, we differentiate Eq. (5) with respect to the logarithm of the total concentration of SAS, keeping the total concentration of NDA constant:

$$
\begin{aligned}
-[\mathrm{d}\gamma/RT\,\mathrm{d}\ln C^{\mathrm{D}}]_{C^{\mathrm{A}}} = \Gamma^{\mathrm{D}}[&(\mathrm{d}\ln C_{\mathrm{D}}/\mathrm{d}\ln C^{\mathrm{D}})_{C^{\mathrm{A}}} \\
&+ (\mathrm{d}\ln C_{\mathrm{Na}}/\mathrm{d}\ln C^{\mathrm{D}})_{C^{\mathrm{A}}}] \\
&+ \Gamma^{\mathrm{A}}(\mathrm{d}\ln C_{\mathrm{A}}/\mathrm{d}\ln C^{\mathrm{D}})_{C^{\mathrm{A}}} \qquad (10)
\end{aligned}
$$

where:

$$C^{\mathrm{A}} = C_{\mathrm{A}} + C_{\mathrm{C}}, \quad C^{\mathrm{D}} = C_{\mathrm{D}} + C_{\mathrm{C}} = C_{\mathrm{Na}} \qquad (11)$$

By substituting Eq. (11) into Eq. (3) and differentiating with respect to C^{D}, while keeping C^{A} constant, the following equations are obtained:

$$(\mathrm{d}C_{\mathrm{D}}/\mathrm{d}C^{\mathrm{D}})_{C^{\mathrm{A}}} = (KC_{\mathrm{D}}+1)/(2KC_{\mathrm{D}}+KC^{\mathrm{A}}-KC^{\mathrm{D}}+1)$$

$$(\mathrm{d}C_{\mathrm{A}}/\mathrm{d}C^{\mathrm{D}})_{C^{\mathrm{A}}} = -KC_{\mathrm{A}}/(2KC_{\mathrm{A}}+KC^{\mathrm{D}}-KC^{\mathrm{A}}+1)$$

which, give at $C^{\mathrm{D}}=C^{\mathrm{A}}$:

$$(\mathrm{d}C_{\mathrm{D}}/\mathrm{d}C^{\mathrm{D}})_{C^{\mathrm{A}},C^{\mathrm{D}}=C^{\mathrm{A}}} = (KC_{\mathrm{D}}+1)/(2KC_{\mathrm{D}}+1) \qquad (12)$$

$$(\mathrm{d}C_{\mathrm{A}}/\mathrm{d}C^{\mathrm{D}})_{C^{\mathrm{A}},C^{\mathrm{D}}=C^{\mathrm{A}}} = -KC_{\mathrm{A}}/(2KC_{\mathrm{A}}+1) \qquad (13)$$

Further, we obtain from Eqs. (3) and (11), with $C^{\mathrm{D}}=C^{\mathrm{A}}$:

$$(C^{\mathrm{D}}/C_{\mathrm{D}}) = (C^{\mathrm{D}}/C_{\mathrm{A}}) = 2KC^{\mathrm{D}}/(-1+\sqrt{1+4KC^{\mathrm{D}}}) \qquad (14)$$

By putting Eqs. (12), (13), (14) and $(\mathrm{d}\ln C_{\mathrm{Na}}/\mathrm{d}\ln C^{\mathrm{D}})_{C^{\mathrm{A}}} = 1$ (from Eq. (11)) into Eq. (10),

$$I_{\mathrm{A},1:1} = (q+1)\Gamma^{\mathrm{D}} - r\Gamma^{\mathrm{A}} \qquad (15)$$

is obtained, where:

$$I_{\mathrm{A},1:1} = -[\mathrm{d}\gamma/RT\,\mathrm{d}\ln C^{\mathrm{D}}]_{C^{\mathrm{A}},C^{\mathrm{D}}=C^{\mathrm{A}}}$$

$$q = KC^{\mathrm{D}}(1+\sqrt{1+4KC^{\mathrm{D}}})/(1+4KC^{\mathrm{D}}-\sqrt{1+4KC^{\mathrm{D}}})$$

$$r = KC^{\mathrm{D}}/\sqrt{1+4KC^{\mathrm{D}}}$$

Equations (9) and (15) finally give:

$$\Gamma^{\mathrm{A}} = [(x^2+6x+1)/2(x+1)^2]I_{1:1} - [(3x+1)/(x+1)^2]I_{\mathrm{A},1:1} \qquad (16)$$

$$\Gamma^{\mathrm{D}} = [(x-1)/2(x+1)]I_{1:1} + [1/(x+1)]I_{\mathrm{A},1:1} \qquad (17)$$

where

$$x = \sqrt{1+4KC^{\mathrm{D}}}$$

By using Eqs. (16) and (17), Γ^{A} and Γ^{D} can be calculated for each system. The values of $I_{1:1}$ in Eqs. (16) and (17) can be obtained from the slopes of the curves for the mixed systems shown in Fig. 1. The values of $I_{\mathrm{A},1:1}$ can be obtained from the slopes of the surface tension *vs.* C^{D} curves at $C^{\mathrm{D}}=C^{\mathrm{A}}$. The curves obtained for NDA–STS, NDA–SDS, and NDA–SDeS systems are shown in Figs. 7 and 8. The arrows in the figures indicate the equimolar concentration of $C^{\mathrm{D}}=C^{\mathrm{A}}$, where the slopes give the respective values of $I_{\mathrm{A},1:1}$ for these systems. Using these data of $I_{1:1}$ and $I_{\mathrm{A},1:1}$, the values of K were determined so as to obtain the best fit between the calculated and observed Γ^{A}'s and Γ^{D}'s.

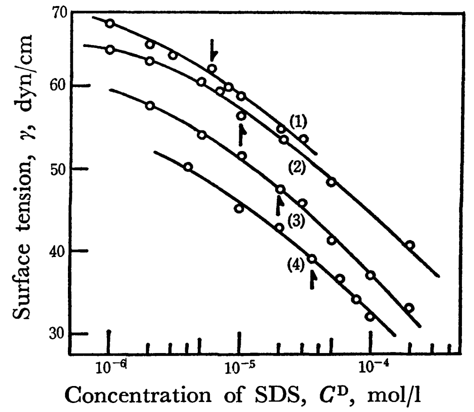

Fig. 7. Surface tension of mixed system *vs.* concentration of SDS.
concentration of NDA (10^{-5} mol/l)
(1): 0.6, (2): 1.0, (3): 2.0, (4): 3.6

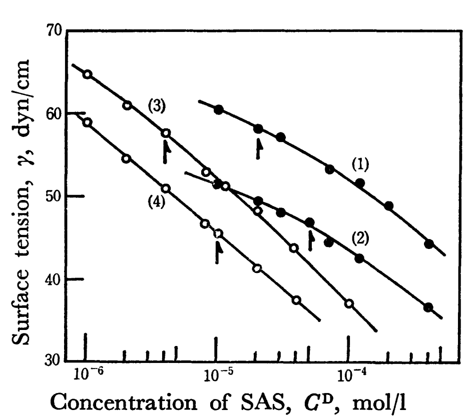

Fig. 8. Surface tension of mixed system *vs.* concentration of SAS.
(●: SDeS, ○: STS).
concentration of NDA (10^{-5} mol/l)
(1): 2.0, (2): 5.0, (3): 0.4, (4): 1.0

The best-fit Γ's thus calculated are shown, together with the observed values, in Figs. 2, 3, and 4.

The values of K were found to be 3.36×10^5, 6.54×10^4, and 1.32×10^4 mol/l for NDA–STS, NDA–SDS, and NDA–SDeS systems respectively. In the case of the interaction of SDS with a cationic surfactant(dodecyltrimethylammonium bromide) with the same hydrocarbon chain length as NDA, the equilibrium constant of complex formation has been determined by conductometry to be 1.67×10^4 mol/l.[2] The overall agreement of those results with ours suggests that the interaction between SAS and the ampholyte NDA is roughly the same in magnitude as that between SAS and the cationic surfactant. The fractions of complex formation in the solution as expressed by $C_{\mathrm{C}}/C^{\mathrm{D}}$ were calculated to be 0.42, 0.55, and 0.70 for NDA–SDeS, NDA–SDS, and NDA–STS systems respectively at a concentration slightly less than the breakpoints of the curves in Fig. 1.

The Free Energy of Complex Formation. Figure 9 shows the relationship between ln K and the number of carbon atoms in the hydrocarbon chain of SAS. A linear relationship with a positive slope is found to hold. This result shows that the interaction between

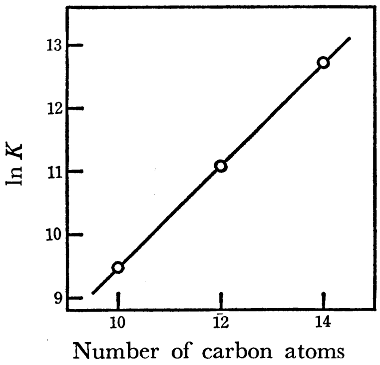

Fig. 9. ln *K* *vs.* number of carbon atoms in hydrocarbon chain of sodium alkylsulfate.

hydrocarbon chains affects the complex formation in addition to the electrostatic interaction. The free energy change in the complex formation calculated according to the $\Delta G^\circ = -RT \ln K$ relation is found to decrease by 0.50 kcal/mol for each increase in the methylene group of SAS. The value can be regarded as the free energy of hydrophobic interaction per mol of the methylene group of the surfactants, since the value is of the same order of magnitude as has been evaluated for amino acid side chains, *i.e.*, −0.5 to −0.6 kcal/mol for the hydrophobic bond.[18] These facts support the 1 : 1-complex formation between NDA and SAS molecules due to ionic and hydrophobic interactions.

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