Radiotracer Studies of the Adsorption of an Ampholytic Surfactant, *N*-dodecyl-*β*-alanine, at the Aqueous Surface

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A tritiated ampholytic surfactant, *N*-dodecyl-*β*-alanine, $C_{10}H_{21}$-$(CHT)_2$-NH_2^+-$(CH_2)_2$-COO^-, was synthesized, and the amount of adsorption on an aqueous surface was measured directly by the radiotracer method. The adsorption isotherm near the neutral pH region showed a saturation value of 3.73×10^{-10} mol/cm^2 above the concentration of about 1/5 of the critical micelle concentration in the absence of added salt, and a value of 4.74×10^{-10} mol/cm^2 above the critical micelle concentration in the presence of 1 mol/l NaCl. In the presence of 1 mol/l NaCl, no effect of pH on the adsorption was found. The Gibbs adsorption isotherm applicable to the aqueous ampholytic surfactant was derived. The observed amounts of adsorption in the presence and absence of NaCl were in good agreement with the values calculated from the Gibbs adsorption isotherm, using the surface tension data measured by the Wilhelmy plate method.

Although the bulk properties of aqueous solutions of ampholytic surfactants have been studied by many investigators,[1–4] the studies of such surface properties of aqueous ampholytic surfactant solutions as surface tension and adsorption are rather rare.[3–4] Especially, no direct measurement of the adsorption of an ampholytic surfactant on an aqueous surface has yet been reported as far as the present authors are aware. Such a measurement of adsorption is important, however, from both theoretical and practical points of view, as in the cases of aqueous anionic and nonionic surfactant solutions previously reported.[5–6]

In the present study, a tritiated ampholytic surfactant, *N*-dodecyl-*β*-alanine(NDA), was synthesized in order to measure the amount of adsorption directly by the radiotracer method, and in order to confirm the applicability of the Gibbs adsorption isotherm derived for an aqueous ampholytic surfactant solution.

Experimental

Materials. Tritiated *N*-dodecyl-*β*-alanine(TNDA) was synthesized according to the following process, the details of which will be reported elsewhere.[7] Tritiated dodecanoic acid(I), obtained by tritiating dodecenoic acid, was allowed to react with urea for five hours at 170—180 °C to form dodecanoic acid amide(II). By the subsequent reduction of (II) using lithium aluminium hydride in ethyl ether, tritiated dodecylamine(III) was obtained. TNDA was obtained by the reaction of (III) with *β*-propiolactone in acetonitrile for an hour at 30 °C.[8] A crude product was purified by repeated recrystallizations from a mixture of acetone and ethyl alcohol (1 : 1), followed by drying in a vacuum. Thin-layer chromatography confirmed the absence of unreacted materials in the final product. The infrared spectra of the product, as well as the nonradioactive one used, confirmed the zwitterionic structure.[2] The specific activity of the sample was about 16 Ci/mol.

Sodium chloride was purified by fusing a comercial extra-pure-grade reagent for five hours in a platinum crucible to remove any surface-active contaminants. The water used for preparing the solutions was obtained by first refluxing ordinarily distilled water with acid permanganate, then distilling it from an alkaline permanganate solution, and finally distilling it twice using a Hysil flask. The hydrochloric acid used for controlling the pH of solutions in the acid region was purified by the distillation of a dilute extra-pure-grade reagent. The sodium hydroxide used for controlling the pH in the alkaline region was purified by the recrystallization of extra-pure-grade reagent from triple-distilled water.

Methods and Procedures. The method and apparatus for the measurements of the adsorption by the radiotracer method were similar to those described previously.[5] The total radioactivity over the surface, R_1, and the radioactivity from the bulk solution, R_2, of an aqueous TNDA solution which had attained an adsorption equilibrium were measured by means of a sheet scintillation counter at 30 °C. The radioactivity corresponding to the adsorbed molecules, $R_1 - R_2$, was calculated and multiplied by a conversion factor to obtain the amount of adsorption.[5,6] To eliminate the effects of atmospheric carbon dioxide and the evaporation of the solution, the measurements were made in a humidified nitrogen atmosphere.

The surface tension was measured by the Wilhelmy plate method.[9] To obtain the equilibrium values, the time dependence of the surface tension was self-recorded, and extrapolated to infinite time.[10] The drop weight method was also used for the sake of comparison.

Results and Discussion

Adsorption of NDA. Figure 1 shows the time dependence of the total radioactivity over the surface of TNDA solutions of various concentrations. The time required for attaining a steady value was about 60 minutes for the solutions studied; this is longer than the time observed for the adsorption of sodium dodecylsulfate(SDS),[5] probably because of the adsorption from a relatively dilute solution in the case of NDA as compared with that of SDS. The steady count rate obtained from Fig. 1 was taken as the equilibrium value, R_1, which is plotted against the NDA concentration in Fig. 2. The concentration dependence of the radioactivity due to the bulk of a solution, R_2, was estimated as a straight line passing through the point of origin with the same inclination as that of the linear part of the R_1 *vs.* concentration curve in Fig. 2, as has been confirmed in the case of the direct measurement of R_2.[5,6] The amount of adsorption, Γ^A, at an aqueous surface is obtained as:

$$\Gamma^A = k(R_1 - R_2)$$

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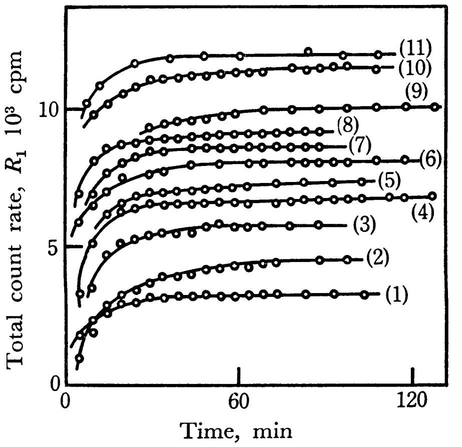

Fig. 1. Time dependence of total radioactivity, R_1, over solution surface.
Concentration of NDA (10^{-5} mol/l)
(1) 0.451 (2) 0.756 (3) 1.06 (4) 1.71
(5) 4.12 (6) 10.7 (7) 17.1 (8) 22.7
(9) 43.0 (10) 85.6 (11) 120.0

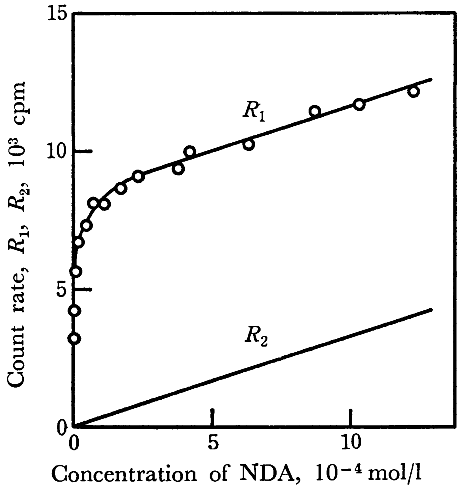

Fig. 2. Total and bulk radioactivities *vs.* concentration.

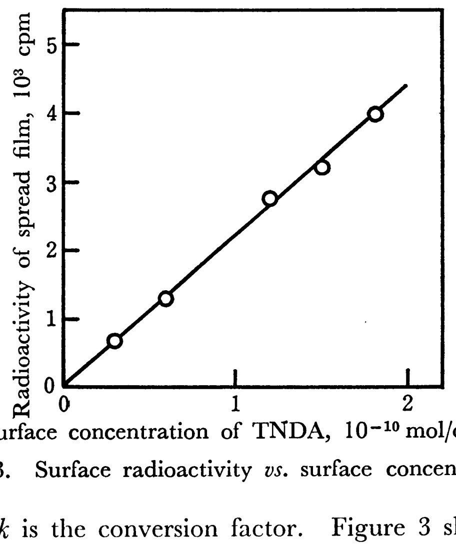

Fig. 3. Surface radioactivity *vs.* surface concentration.

where k is the conversion factor. Figure 3 shows the relation between the surface concentration of TNDA spread on the surface of a saturated ammonium nitrate solution and the radioactivity due to the spread film. The k value was calculated from the slope as 4.55×10^{-14} mol/cm^2/cpm.

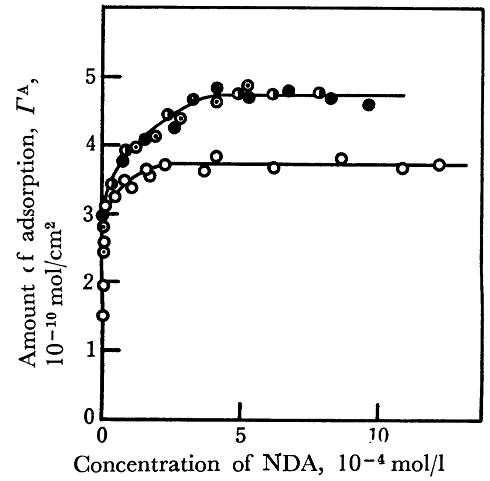

Fig. 4. Adsorption of NDA at aqueous surface.
Addition of ○: 0 mol/l NaCl, near neutral pH, ●: 1 mol/l NaCl, near neutral pH ⊙: 1 mol/l NaCl, pH 2.0 ◑: 1 mol/l NaCl, pH 12.0

The amounts of adsorption, Γ^A, with and without added salt plotted against the concentration of NDA near a neutral pH are shown in Fig. 4. The amounts of adsorption increase with the concentration and attain saturated value of 3.73×10^{-10} mol/cm^2 above a concentration of about 2×10^{-4} mol/l in the absence of added salt, and value of 4.74×10^{-10} mol/cm^2 above a concentration of about 4×10^{-4} mol/l in the presence of 1 mol/l NaCl.

The effect of the pH on the adsorption was studied further, since an ampholytic surfactant was expected to be sensitive to changes in the pH. However, the adsorption isotherm for the NDA systems of pH 2 and 12 in the presence of 1 mol/l NaCl showed no detectable change in the amount of adsorption, as is shown in Fig. 4. This may be explained as being due to the contraction of the ionic atmosphere around the polar head caused by the addition of concentrated NaCl, which makes NDA less ionic in nature.

In Table 1, the saturated amount of adsorption of NDA near the neutral pH obtained in the present study is compared with that of sodium dodecylsulfate(SDS),[5] an anionic surfactant, or hexaoxyethylenedodecylmonoether(D(EO)$_6$),[6] a nonionic surfactant, with equal lengths of the hydrocarbon chain. The amount is larger for NDA than for the other two substances, perhaps because of the neutralization of the charges of the NDA polar head groups by intra- and/or inter-

TABLE 1. SATURATED AMOUNT OF ADSORPTION NEAR NEUTRAL pH

Surfactants	Amount of adsorption (10^{-10} mol/cm^2)
NDA	3.73 (30 °C)
SDS	3.19 (25 °C)[5]
D(EO)$_6$	2.73 (30 °C)[6]

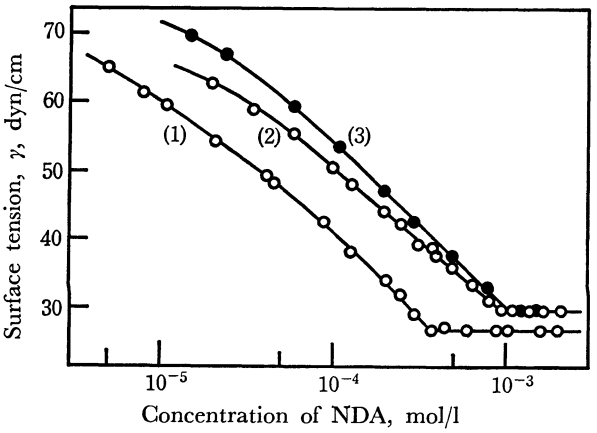

Fig. 5. Surface tension *vs.* concentration of NDA curve.
(1) presence of 1 mol/l NaCl (Wilhelmy plate method)
(2) absence of added salt (Wilhelmy plate method)
(3) absence of added salt (drop weight method)

molecular salt formation in the isoelectric region.

Surface Tension. Figure 5 shows the curves of the surface tension *vs.* the concentration of NDA with and without 1 mol/l NaCl. It may be seen in Fig. 5 that, in the absence of added salt, the slope is constant in the region of NDA concentrations from about 2×10^{-4} mol/l to the CMC, while in the presence of added salt the slope gradually increases up to the CMC. The data obtained by the drop weight method in the former case are also plotted in Fig. 5 as filled circles. It may be seen that the values obtained by the drop weight method are higher than those obtained by the Wilhelmy method; the former values cannot be used for further calculation, as will be discussed later.

The Gibbs Adsorption Isotherm. The Gibbs adsorption isotherm is written, in a general form, as[11]

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

where γ denotes the surface tension, and Γ_i and a_i, the surface excess and the activity of the i'th solute respectively.

1. *The Case of the Absence of Added Salt*: Equation (1) may be rewritten for an ampholytic surfactant solution as:

$$-\mathrm{d}\gamma/RT = \Gamma_{\mathrm{A}^\pm}\,\mathrm{d}\ln C_{\mathrm{A}^\pm} + \Gamma_{\mathrm{A}^+}\,\mathrm{d}\ln C_{\mathrm{A}^+} + \Gamma_{\mathrm{A}^-}\,\mathrm{d}\ln C_{\mathrm{A}^-} + \Gamma_{\mathrm{H}^+}\,\mathrm{d}\ln C_{\mathrm{H}^+} + \Gamma_{\mathrm{OH}^-}\,\mathrm{d}\ln C_{\mathrm{OH}^-} \tag{2}$$

where the subscripts $\mathrm{A}^\pm$, A^+, A^-, H^+ and OH^- refer to the zwitterion, the cation, the anion of the ampholyte NDA, the hydrogen ion, and the hydroxide ion respectively. Since the concentration of the surfactant used is of the order of magnitude of 10^{-4} mol/l, the acitivity terms in Eq. (2) may safely be replaced by the concentration.

Further, we obtain the following relations:

$$K_1 = C_{\mathrm{A}^\pm}C_{\mathrm{H}^+}/C_{\mathrm{A}^+} \tag{3}$$

$$K_2 = C_{\mathrm{A}^-}C_{\mathrm{H}^+}/C_{\mathrm{A}^\pm} \tag{4}$$

$$K_{\mathrm{w}} = C_{\mathrm{H}^+}C_{\mathrm{OH}^-} \tag{5}$$

$$\Gamma_{\mathrm{A}^+} + \Gamma_{\mathrm{H}^+} = \Gamma_{\mathrm{A}^-} + \Gamma_{\mathrm{OH}^-} \tag{6}$$

where K_1 and K_2 express the first and second dissociation constants of NDA, considered as a dibasic acid, and K_{w}, the dissociation constant of the water. Equation (6) represents the electrical neutrality of the adsorbed ionic species. By substituting the logarithmic forms of Eqs. (3) and (4) into Eq. (2), we obtain:

$$-\mathrm{d}\gamma/RT = (\Gamma_{\mathrm{A}^\pm}+\Gamma_{\mathrm{A}^+}+\Gamma_{\mathrm{A}^-})\,\mathrm{d}\ln C_{\mathrm{A}^\pm} + (\Gamma_{\mathrm{A}^+}-\Gamma_{\mathrm{A}^-}+\Gamma_{\mathrm{H}^+})\,\mathrm{d}\ln C_{\mathrm{H}^+} + \Gamma_{\mathrm{OH}^-}\,\mathrm{d}\ln C_{\mathrm{OH}^-} \tag{7}$$

Here, we used these notations:

$$\Gamma^{\mathrm{A}} = \Gamma_{\mathrm{A}^\pm} + \Gamma_{\mathrm{A}^+} + \Gamma_{\mathrm{A}^-} \tag{8}$$

as the total adsorption amount of NDA, and

$$C^{\mathrm{A}} = C_{\mathrm{A}^\pm} + C_{\mathrm{A}^+} + C_{\mathrm{A}^-} \tag{9}$$

as the total bulk concentration of NDA. By substituting Eqs. (5), (6) and (8) into Eq. (7) we obtain:

$$-\mathrm{d}\gamma/RT = \Gamma^{\mathrm{A}}\,\mathrm{d}\ln C_{\mathrm{A}^\pm} \tag{10}$$

Further, from Eqs. (3), (4) and (9) we obtain this relation:

$$\mathrm{d}\ln C_{\mathrm{A}^\pm} = \mathrm{d}\ln C^{\mathrm{A}} + [(C_{\mathrm{A}^-}-C_{\mathrm{A}^+})/C^{\mathrm{A}}]\,\mathrm{d}\ln C_{\mathrm{H}^+}$$

which, together with Eq. (10), gives:

$$-\mathrm{d}\gamma/RT\,\mathrm{d}\ln C^{\mathrm{A}} = \Gamma^{\mathrm{A}}[1+K(\mathrm{d}\ln C_{\mathrm{H}^+}/\mathrm{d}\ln C^{\mathrm{A}})] \tag{11}$$

where:

$$K = (C_{\mathrm{A}^-}-C_{\mathrm{A}^+})/C^{\mathrm{A}}$$

On the other hand, using Eqs. (3), (4), and (9), we obtain:

$$K = (K_1K_2-C^2_{\mathrm{H}^+})/(C^2_{\mathrm{H}^+}+K_1C_{\mathrm{H}^+}+K_1K_2) \tag{12}$$

In the pH region near the isoelectric point, the second term in the brackets of Eq. (11) is calculated using these experimental data: $K_1=3.1\times 10^{-4}$, $K_2=1.3\times 10^{-10}$ mol/l, $C_{\mathrm{H}^+}=10^{-6}$ mol/l and ($\mathrm{d}\ln C_{\mathrm{H}^+}$ $\mathrm{d}\ln C^{\mathrm{A}}$)$<0.1$ for the present experimental conditions of $C^{\mathrm{A}}=10^{-4}$ to 10^{-3} mol/l. The order of magnitude is about 10^{-4}, which is negligible compared with unity. Thus, Eq. (11) can eventually be reduced for the NDA solution to a simple form,

$$\Gamma^{\mathrm{A}} = -\mathrm{d}\gamma/RT\,\mathrm{d}\ln C^{\mathrm{A}} \tag{13}$$

2. *The Case of the Presence of Excess Added Salt*: In the presence of excess NaCl (1 mol/l in the present study) Eq. (1) still holds, since $\mathrm{d}\ln C_{\mathrm{Na}^+}=0$, and $\mathrm{d}\ln C_{\mathrm{Cl}^-}=0$. Therefore, the calculations are the same as in the case of Eqs. (1) to (5). The electrical neutrality of the adsorbed ionic species is expressed, instead of Eq. (6), as:

$$\Gamma_{\mathrm{Na}^+} + \Gamma_{\mathrm{A}^+} + \Gamma_{\mathrm{H}^+} = \Gamma_{\mathrm{Cl}^-} + \Gamma_{\mathrm{A}^-} + \Gamma_{\mathrm{OH}^-}$$

Therefore, the equation corresponding to Eq. (10) may be written as:

$$-\mathrm{d}\gamma/RT = \Gamma^{\mathrm{A}}\,\mathrm{d}\ln C_{\mathrm{A}^\pm} + (\Gamma_{\mathrm{Cl}^-}-\Gamma_{\mathrm{Na}^+})\,\mathrm{d}\ln C_{\mathrm{H}^+}$$

and Equation:

$$-\mathrm{d}\gamma/RT\,\mathrm{d}\ln C^{\mathrm{A}} = \Gamma^{\mathrm{A}} + (K\Gamma^{\mathrm{A}}+\Gamma_{\mathrm{Cl}^-}-\Gamma_{\mathrm{Na}^+}) \times (\mathrm{d}\ln C_{\mathrm{H}^+}/\mathrm{d}\ln C^{\mathrm{A}}) \tag{14}$$

is obtained instead of Eq. (11).

It should be noted that Eq. (14) holds also for the system in the presence of HCl or NaOH so long as NaCl is present in a larger amount than the other solute. Therefore, if the pH is also kept, or happens to be constant, the second term of Eq. (14) may drop and a simple equation may result:

$$\Gamma^{A} = -(\mathrm{d}\gamma/RT\,\mathrm{dln}\,C^{A})_{\mathrm{pH,\ excess\ NaCl}} \qquad (15)$$

The condition of Eq. (15) was actually satisfied for the ampholyte NDA containing excess NaCl without added acid or alkali.

Calculation of the Adsorption Amount by Means of the Gibbs Adsorption Isotherm. The amount of adsorption, calculated from the data of Fig. 5 by applying Eqs. (13) and (15), is shown by Curves A, B and C in Fig. 6. The figure also contains, for the sake of comparison, the results by Durham[4] by the use of the drop weight method (Curve D). It may be seen that the values obtained by the radiotracer method for the systems both with and without added salt are in good agreement with those calculated from the data obtained by the Wilhelmy plate method (A and C). The values calculated from the data obtained by the drop weight method (B and D) are, however, distinctly higher than the observed ones. The disagreement of the values obtained by the drop-weight method may be ascribed to the application of the Gibbs adsorption isotherm to the nonequilibrium surface tension data.

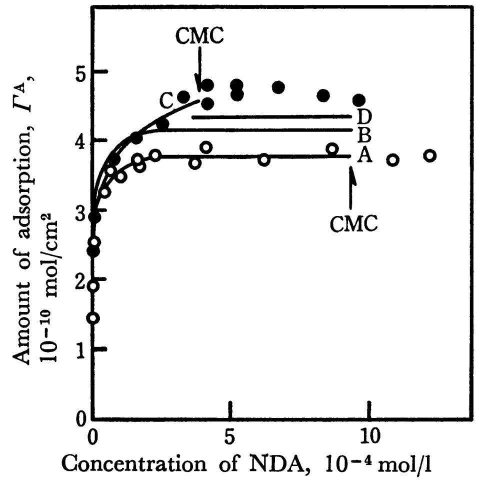

Fig. 6. Observed and calculated values.
Observed values: ○; in the absence of added salt ●; in the presence of 1 mol/l NaCl
Calculated values: in the absence of NaCl; (A) Wilhelmy plate method, (B), (D)[4] drop weight method, in the presence of 1 mol/l NaCl; (C) Wilhelmy plate method.

Thus, the agreement between the calculated and observed values indicates the validity of the Gibbs adsorption isotherm derived in the present study. It is confirmed experimentally that, for aqueous ampholytic surfactant solutions in an isoelectric region, where $K_1K_2 \doteqdot C^2_{\mathrm{H}^+}$ and where, therefore, $K \doteqdot 0$, the Gibbs adsorption isotherm is applicable in a form similar to that used for a nonionic surfactant.[6] This can be also explained by the quasi-nonionic nature of the ampholytic surfactant NDA due to the intra- and/or intermolecular neutralization of the charges of polar heads in the solution of its isoelectric region, as has been pointed out with regard to the dependence of the critical micelle concentration on the temperature and added salt,[2] and with regard to a relatively large amount of the saturated adsorption of NDA mentioned above.

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