BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1767—1771 (1971)

Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. III. The Effects of Salt on the Adsorption of Sodium Dodecylsulfate

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(Received January 25, 1971)

The adsorbed amounts were measured on the surface of aqueous solutions containing tritiated sodium dodecylsulfate (TSDS) and varying amounts of NaCl by the direct radiotracer method. The surface tensions were also measured for the same solutions by the drop-volume method. The Gibbs adsorption isotherm, derived without assuming the adsorption of the chloride ion, was applied, and the amounts of adsorption were calculated for both dodecylsulfate and chloride ions. The observed amounts of dodecylsulfate adsorption were confirmed to be in good agreement with those calculated, and the calculated amounts of chloride adsorption turned out to be nearly zero or slightly negative, which is usually theoretically assumed because of the ionic repulsion due to the adsorbed dodecylsulfate. Further, the adsorption of the dodecylsulfate ion attained a constant and saturate value beyond a certain concentration (SAC) below the critical micelle concentration (CMC). The logarithms of SAC were found to vary linearly with the logarithms of CMC for the range of salt concentration studied. The value of SAC being in a close relation with the surface phenomena is considered to be another measure of the surface activity of surfactants.

There have been many studies to check the validity of the Gibbs adsorption isotherm.[1-5] By a radiotracer method, we have also experimentally confirmed that the adsorption of the ionic surfactants on an aqueous surface from their solution takes place in accordance with the Gibbs equation both in the absence of and in the presence of in an excess amount of an inorganic salt having a cation in common.[6,7] However, there has no paper dealing with the direct measurement of adsorption at the air-solution interface of the ionic surfactant as a function of the concentration of the coexisting salt. Matijevic and Pethica,[8] though, derived a Gibbs ad-

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[1] J. W. McBain and L. A. Wood, *Proc. Roy. Soc.* (London), **A174**, **286** (1940).

[2] A. P. Brady, *J. Phys. Chem.*, **53**, 56 (1949).

[3] J. T. Davies, *Trans. Faraday Soc.*, **48**, 1052 (1952).

[4] B. A. Pethica, *ibid.*, **50**, 413 (1954).

[5] R. Matuura, H. Kimizuka, S. Miyamoto, and R. Shimozawa, This Bulletin, **31**, 532 (1958).

[6] K. Tajima, M. Muramatsu, and T. Sasaki, *ibid.*, **43**, 1991 (1970).

[7] K. Tajima, *ibid.*, **43**, 3063 (1970).

[8] E. Matijevic and B. A. Pethica, *Trans. Faraday Soc.*, **54**, 1382 (1958).

sorption isotherm which can be applied to the solution of sodium dodecylsulfate (SDS) in the presence of sodium chloride, and calculated the adsorbed amount of the dodecylsulfate ion from the surface-tension concentration relation of the solution. In their derivation of the adsorption equation, they assumed that the excess of the chloride ion at the surface is negligible in amount. This assumption, although acceptable from the theoretical viewpoint,[9] has not been confirmed experimentally.

In the present paper, the Gibbs adsorption isotherm is applied from a more general viewpoint, with no preliminary assumption of the adsorbed amount of solute ions in the solution and with activity in place of concentration. The validity of the adsorption equation thus derived is confirmed by the direct measurement of the amount of adsorption by a radio-tracer method.

Theoretical

The Gibbs adsorption isotherm[10] is written, in a general form, as:

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

where γ represents the surface tension, and Γ_i and a_i, the surface excess and the activity of the ith ionic species in solution respectively. Assuming that the bulk solution is electrically neutral as a whole and that surface hydrolysis is absent (bulk hydrolysis was confirmed to be absent, as judged from the pH being unaffected by the dissolution of SDS), Eq. (1) is rewritten for the SDS solution containing sodium chloride as:

$$\begin{aligned}-\mathrm{d}\gamma = {}& RT\Gamma_{\mathrm{Na}^+}\mathrm{d}\ln a_{\mathrm{Na}^+} + RT\Gamma_{\mathrm{D}^-}\mathrm{d}\ln a_{\mathrm{D}^-}\\ &+ RT\Gamma_{\mathrm{Cl}^-}\mathrm{d}\ln a_{\mathrm{Cl}^-}\end{aligned} \tag{2}$$

where the three subscripts Na$^+$, D$^-$, and Cl$^-$ denote sodium, dodecylsulfate, and chloride ions respectively. Using the activity coefficient and the concentration instead of the activity, and differentiating Eq. (2) with respect to C_{D^-}, while keeping the concentration of NaCl constant (therefore, d C_{Na^+}=d C_{D^-}), we obtain the following equation:

$$\begin{aligned}-\left(\frac{\mathrm{d}\gamma}{RT\mathrm{d}\ln C_{\mathrm{D}^-}}\right)_{\mathrm{NaCl}} = {}& \Gamma_{\mathrm{Na}^+}\frac{C_{\mathrm{D}^-}}{C_{\mathrm{Na}^+}} + \Gamma_{\mathrm{D}^-}\\ &+ 2\Gamma_{\mathrm{Cl}^-}\frac{\mathrm{d}\ln f_\pm^{\mathrm{NaCl}}}{\mathrm{d}\ln C_{\mathrm{D}^-}} + 2\Gamma_{\mathrm{D}^-}\frac{\mathrm{d}\ln f_\pm^{\mathrm{NaD}}}{\mathrm{d}\ln C_{\mathrm{D}^-}}\end{aligned} \tag{3}$$

where C's denote the concentration of the ions specified and $f_\pm{}^{\mathrm{NaCl}}$ and $f_\pm{}^{\mathrm{NaD}}$, the mean activity coefficients of NaCl and SDS respectively. Similarly, differentiating Eq. (2) with respect to C_{Cl^-} while keeping the concentration of NaD constant, we obtain:

$$\begin{aligned}-\left(\frac{\mathrm{d}\gamma}{RT\mathrm{d}\ln C_{\mathrm{Cl}^-}}\right)_{\mathrm{NaD}} = {}& \Gamma_{\mathrm{Na}^+}\frac{C_{\mathrm{Cl}^+}}{C_{\mathrm{Na}^+}}\\ &+ 2\Gamma_{\mathrm{D}^+}\frac{\mathrm{d}\ln f_\pm^{\mathrm{NaCl}}}{\mathrm{d}\ln C_{\mathrm{Cl}^-}} + 2\Gamma_{\mathrm{Cl}^-}\frac{\mathrm{d}\ln f_\pm^{\mathrm{NaD}}}{\mathrm{d}\ln C_{\mathrm{Cl}^-}}\end{aligned} \tag{4}$$

Putting

$$\frac{\mathrm{d}\ln f_\pm^{\mathrm{NaCl}}}{\mathrm{d}\ln C_{\mathrm{D}^-}} = \frac{\mathrm{d}\ln f_\pm^{\mathrm{NaD}}}{\mathrm{d}\ln C_{\mathrm{D}^-}} \equiv \alpha$$

$$\frac{\mathrm{d}\ln f_\pm^{\mathrm{NaCl}}}{\mathrm{d}\ln C_{\mathrm{Cl}^-}} = \frac{\mathrm{d}\ln f_\pm^{\mathrm{NaD}}}{\mathrm{d}\ln C_{\mathrm{Cl}^-}} \equiv \beta$$

and using the notations:

$$\frac{C_{\mathrm{D}^-}}{C_{\mathrm{Na}^+}} = a,\quad \frac{C_{\mathrm{Cl}^-}}{C_{\mathrm{Na}^+}} = b \tag{5}$$

$$\left.\begin{aligned}-\left(\frac{\mathrm{d}\gamma}{RT\mathrm{d}\ln C_{\mathrm{D}^-}}\right)_{\mathrm{NaCl}} &= I_{\mathrm{Cl}^-}\\ -\left(\frac{\mathrm{d}\gamma}{RT\mathrm{d}\ln C_{\mathrm{Cl}^-}}\right)_{\mathrm{NaD}} &= I_{\mathrm{D}^-}\end{aligned}\right\} \tag{6}$$

Eqs. (3) and (4) are then rewritten as:

$$I_{\mathrm{Cl}^-} = \Gamma_{\mathrm{Cl}^-}(a+2\alpha) + \Gamma_{\mathrm{D}^-}(1+a+2\alpha) \tag{7}$$

$$I_{\mathrm{D}^-} = \Gamma_{\mathrm{D}^-}(b+2\beta) + \Gamma_{\mathrm{Cl}^-}(1+b+2\beta) \tag{8}$$

From the condition of electric neutrality at the surface of the solution, we further obtain:

$$\Gamma_{\mathrm{Na}^+} = \Gamma_{\mathrm{D}^-} + \Gamma_{\mathrm{Cl}^-} \tag{9}$$

by combining Eqs. (7), (8), and (9), we have:

$$\Gamma_{\mathrm{Na}^+} = \frac{1}{2(1+\alpha+\beta)}(I_{\mathrm{D}^-} + I_{\mathrm{Cl}^-}) \tag{10}$$

$$\Gamma_{\mathrm{D}^-} = \frac{1}{2(1+\alpha+\beta)}[I_{\mathrm{Cl}^-}(1+b+2\beta) - I_{\mathrm{D}^-}(a+2\alpha)] \tag{11}$$

$$\Gamma_{\mathrm{Cl}^-} = \frac{1}{2(1+\alpha+\beta)}[I_{\mathrm{D}^-}(1+a+2\alpha) - I_{\mathrm{Cl}^-}(b+2\beta)] \tag{12}$$

Estimating the activity coefficient of NaCl and SDS by using the limiting law of the Debye-Hückel theory, as in the previous paper,[7] the values of α and β are given as:

$$2\alpha = -aA\sqrt{C_{\mathrm{Na}^+}} \tag{13}$$

$$2\beta = -bA\sqrt{C_{\mathrm{Na}^+}} \tag{14}$$

where A is the constant in the Debye-Hückel limiting equation, which takes the value of 1.18 at 25°C. By substituting Eqs. (13) and (14) into Eqs. (10), (11), and (12), we obtain:

$$\Gamma_{\mathrm{Na}^+} = \frac{1}{1+i}(I_{\mathrm{Cl}^-} + I_{\mathrm{D}^-}) \tag{15}$$

$$\Gamma_{\mathrm{D}^-} = \frac{1}{1+i}[I_{\mathrm{Cl}^-}(1+bi) - I_{\mathrm{D}^-}ai] \tag{16}$$

$$\Gamma_{\mathrm{Cl}^-} = \frac{1}{1+i}[I_{\mathrm{D}^-}(1+ai) - I_{\mathrm{Cl}^-}bi] \tag{17}$$

where:

$$i = 1 - A\sqrt{C_{\mathrm{Na}^+}} \tag{18}$$

expresses the activity coefficient of the uni-univalent ion at a sufficiently dilute solution and is equal to unity when the mean activity coefficient is unity. It is worth noting that Γ_{D^-} and Γ_{Cl^-} can be separately calculated by Eqs. (16) and (17), if i is calculated according to Eq. (18), and that I_{Cl^-}, I_{D^-}, a and b are calculated from the γ *vs.* C_{NaCl} or γ *vs.* C_{NaD} curves (Eq. (5)) and from Eq. (6). The validity of Eq. (16) can be checked by comparing the value of Γ_{D^-} thus calculated with that measured directly by a radiotracer method for the solutions containing both SDS and NaCl. Further, by putting $\Gamma_{\mathrm{Cl}^-}=0$ and $i=1$, Eqs. (16) and (17) give the same

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[9] E. J. W. Verwey and J. Th. G. Overbeek., "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Co., Amsterdam (1948).

[10] E. A. Guggenheim, "Thermodynamics, " North Holland Publishing Co., Amsterdam (1949).

equation as Matijevic and Pethica's. Here, we are in a position to check experimentally whether or not the theoretical assumption of $\Gamma_{Cl^-}=0$ in their derivation of the equation is valid.

Experimental

The tritiated sodium dodecylsulfate (TSDS) and sodium chloride were the same substances as those used in a previous paper.[7] The surface tension of solutions containing NaCl and SDS was measured by the drop-volume method, and Harkins and Brown's correction[11] was applied. The value of Γ_{D^-} was also measured directly by a radiotracer method using a sheet scintilation counter. The details of the measurements were the same as those described in preceding paper.[6,7] The pH of the bulk solutions was controled at 6±0.2 (25.0°C).

Results and Discussion

Adsorption Isotherm. Figure 1 shows the adsorption isotherms of SDS measured by the radiotracer method at the surface of an aqueous solution containing various concentrations of sodium chloride. Figures 2 and 3 show the curves of γ *vs.* log C_{D^-}, with C_{Cl^-} kept constant for the former and of γ *vs.* log C_{Cl^-}, with C_{D^-} kept constant for the latter. In Figs. 4a, b, and c, the observed values of Γ_{D^-} and those calculated by applying Eqs. (16) and (17) to the data of Figs. 2 and 3 are shown as circles and solid lines respectively. The broken lines in these figures show the values of Γ_{D^-}, which are calculated by assuming $i=1$ in Eq. (16). It may be seen in these figures that the values of Γ calculated from Eqs. (16) and (17) (solid lines) are, as a whole in good agreement, with the observed values except for the adsorption at low concentrations of SDS and NaCl. The broken lines ($i=1$) gradually deviate from both solid lines and observed Γ_{D^-} values in the region of a large concentration of SDS. As for the deviation of solid lines from the observed values of adsorption in a dilute solution of SDS, a similar tendency was also observed in the case of the salt-free SDS solution, where the surface tension used for the calculation was also measured by a drop-volume method. It should be noted that different surface tension values are obtained for the salt-free SDS solution when it is measured by the drop-volume and Wilhelmy plate methods. Therefore, in the case of a low NaCl concentration, such as in Fig. 4a, we should use the surface tension data, as measured by the Wilhelmy plate method to be described below. Unfortunately, the γ *vs.* C_{D^-} relation measured by the Wilhelmy plate method is lacking for the SDS solution with a 1×10^{-3} mol/l NaCl concentration. It can, however, be obtained graphi-

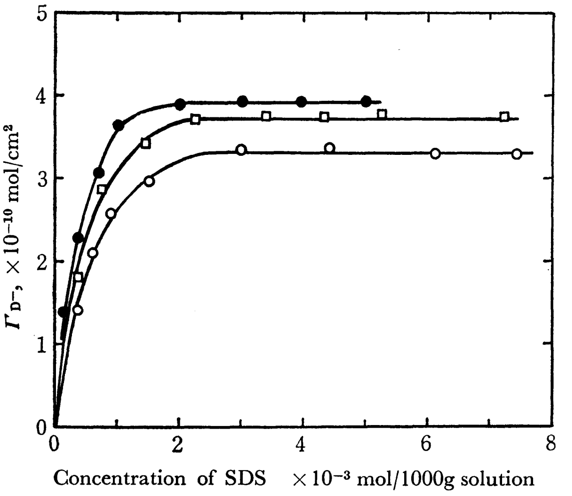

Fig. 1. Adsorption isotherms of SDS solutions in the presence of NaCl at 25°C.

—○—: 1.0×10^{-3} M NaCl
—□—: 5.0×10^{-3} M NaCl
—●—: 10.0×10^{-3} M NaCl

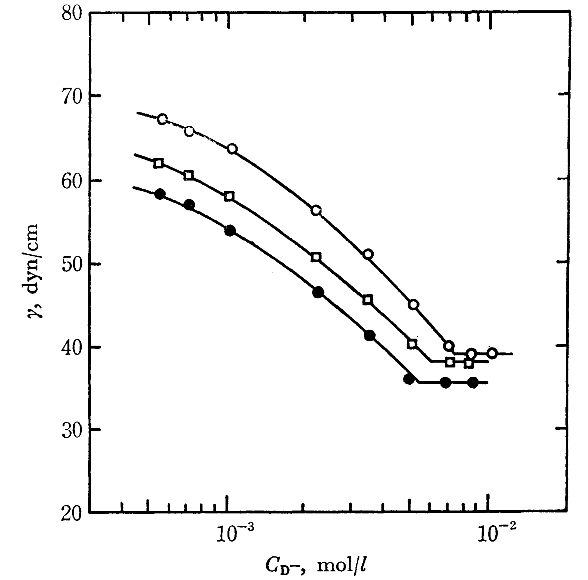

Fig. 2. Surface tensions of SDS solutions in the presence of NaCl at 25°C.

—○—: 1.0×10^{-3} M NaCl
—□—: 5.0×10^{-3} M NaCl
—●—: 10.0×10^{-3} M NaCl

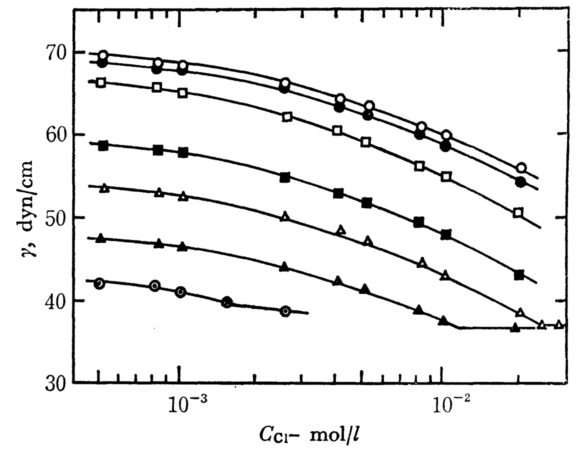

Fig. 3. Surface tensions of NaCl solutions in the presence of SDS at 25°C.

—○—: 0.545×10^{-3} M SDS —●—: 0.698×10^{-3} M SDS
—□—: 1.01 ×10^{-3} M SDS —■—: 2.21 ×10^{-3} M SDS
—△—: 3.48 ×10^{-3} M SDS —▲—: 5.01 ×10^{-3} M SDS
—⊙—: 6.65 ×10^{-3} M SDS

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[11] W. D. Harkins and F. E. Brown, *J. Amer. Chem. Soc.*, **41**, 4499 (1919).

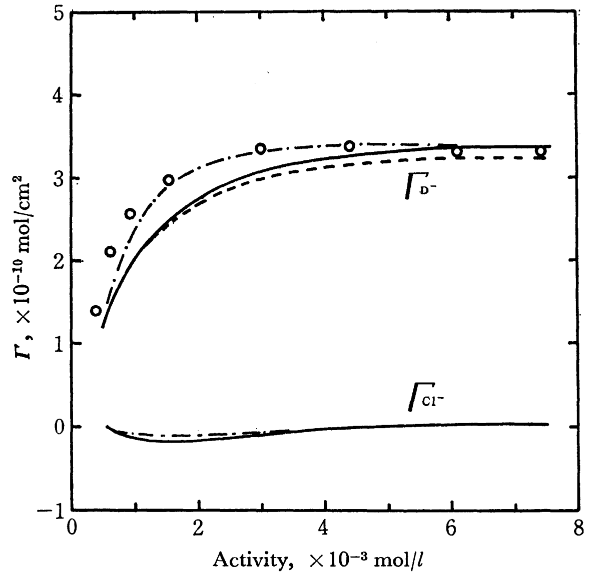

Fig. 4 a: 1.0×10^{-3} M NaCl

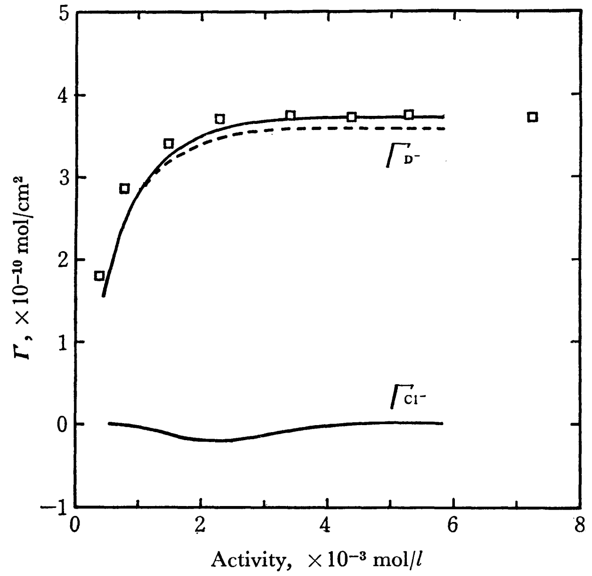

Fig. 4 b: 5.0×10^{-3} M NaCl

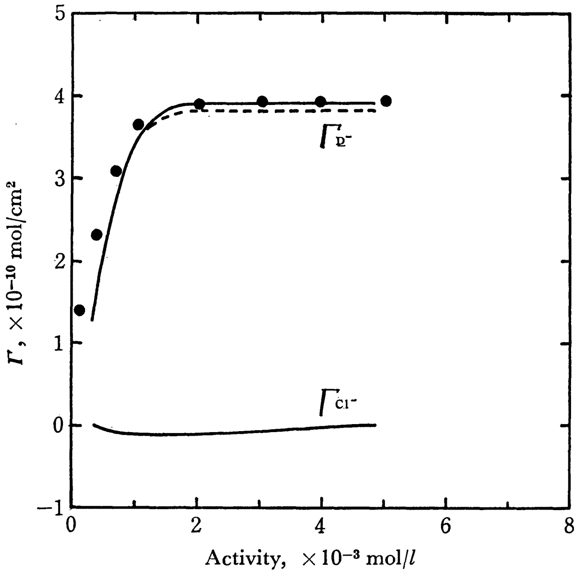

Fig. 4 c: 10.0×10^{-3} M NaCl

Fig. 4. Adsorption isotherms of Γ_{D^-} and Γ_{Cl^-} at the surface of aqueous solutions containing SDS and NaCl.

——: calculated from Eqs. (16) and (17)
------: calculated from Eq. (16) putting $i=1$
-·-·-·: calculated by interpolation (see text)
○, □, ●: observed values

cally by an interpolation, of the γ *vs.* C_{D^-} data for the SDS solution measured by the Wilhelmy plate method, reported in a previous paper.⁶⁾ From the γ *vs.* log-C_{D^-} relation thus obtained and from the γ *vs.* $\log C_{Cl^-}$ relation similarly obtained, Γ_{D^-} and Γ_{Cl^-} can be calculated by applying Eqs. (16) and (17). The results are shown by a chain line in Fig. 4a. It is evident that the chain line is in better agreement with observed values than a solid line would be. Thus, it is confirmed that the Wilhelmy plate method always offers correct values of the surface tension for the calculation of the amount of adsorption, while the drop-volume method gives incorrect values, the error becoming smaller at ionic strengths larger than about 10×10^{-3} mol/l. This may be due to the rapid surface aging at a higher ionic concentration, which makes it possible to obtain an almost equilibrium value of the surface tension at a relatively short time of measurement.

Now, it should be noted that, although the non-adsorption of the chloride ion at an aqueous surface can be theoretically anticipated for aqueous solution containing SDS and NaCl, the experimental evidence has been lacking. The results of the present studies empirically confirm the almost zero value or a slightly negative value of Γ_{Cl^-} as is shown in Figs. 4a, b, and c, although the values of Γ_{Cl^-} in the solution with a lower SDS concentration involve some uncertainties similar to those of Γ_{Cl^-} in dilute solutions. It may be seen that the values of Γ_{D^-} (broken lines) calculated from Eq. (16), assuming $i=1$, agree closely within the limits of experimental error with those obtained by the Matijevic and Pethica equation, which assumes $\Gamma_{Cl^-}=0$ ($i=1$). This agreement confirms the $\Gamma_{Cl^-}=0$ assumption to be valid as far as the calculation of Γ_{D^-} according to Matijevic and Pethica equation is concerned. However, as for the calculation of Γ_{Cl^-}, small but distinct negative values are indicated, and Eqs. (16) and (17) are better applied to the calculation of the adsorption from the solution of two mixed surfactants containing a common cation, although the additional measurements shown in Fig. 3 are required for the calculation of Γ_{Cl^-} and Γ_{D^-}. In this connection, it may be inferred that Dixon *et al.*¹²⁾ made a mistake in calculating the amounts of the adsorption of Aerosol OT and Aerosol OTN at the surface of their mixed solution. They treated the two solutes as independent of each other and used simply:

$$\Gamma_{OT} = I_{OTN}, \qquad \Gamma_{OTN} = I_{OT} \tag{19}$$

where Γ_{OTN}, I_{OTN}, *etc.* denote the corresponding quantities shown in Eq. (6), with D and Cl replaced by OT and OTN respectively. However, since the system

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12) J. K. Dixon, C. M. Judson, and D. J. Salley, "Monomolecular Layers," H. Sobotka, Ed., p. 81, Am. Assoc, Advsn. Sci., Washington, D. C. (1954).

Table 1. Γ_s and A values for saturated adsorption on aqueous NaCl solution (25°C)

C_{NaCl} $\times 10^3$ M	CMC $\times 10^3$M	SAC $\times 10^3$M	Γ_s $\times 10^{10}$mol/m^2	A A^2/molec.
0[a]	8.12	3.1	3.19	52.0
1.0	7.50	3.0	3.31	50.2
5.0	5.80	2.6	3.75	44.3
10.0	5.10	2.0	3.90	42.6
115.0[b]	1.62	0.50	4.33	38.4

a) Ref. 6
b) Ref. 7

contains the Na$^+$ ion in common, we must use equations with the form of Eqs. (16) and (17) instead of Eq. (19).

Saturated Adsorption. The values of the saturated adsorption, Γ_S, of the dodecylsulfate ion in various concentrations of coexisting sodium chloride, together with the corresponding value of the molecular area, are shown in Table 1. A decrease in the molecular area, A, due to the increase in the concentration of sodium chloride is seen; it can be qualitatively interpreted as the effect of added salt on diffuse double layers of the adsorbed ion. The value of SAC, which is the bulk concentration beyond which Γ_S shows a constant and saturate value, is listed in the third column of Table 1. This SAC, which is smaller than the CMC (critical micelle concentration), was determined more accurately by the isotherm (Fig. 1) obtained by the radiotracer method. The correlation between SAC and CMC gives a good linearity, as is shown in Fig. 5. This linearity is expressed as;

$$\log \mathrm{SAC} = 1.16 \log \mathrm{CMC} - 0.04 \tag{20}$$

The value of SAC is confirmed to be about 30—40% of the CMC for all the concentrations of NaCl studied in the present experiments. Van Voorst Vader[13] has reported that the adsorption amount of the ionized surfactant in the aqueous solution is approximately constant within the concentration range of 20—30% of the CMC when the inorganic salt is present. Further, even in another report[14] which insists on a continuous increase in the surfactant adsorption up to the CMC in the presence of salt, the surface tension *vs.* log concentration relation for the surfactant solution does not deviate appreciably from the linear relationship in the range of 30% of the CMC. Accordingly, a constant adsorption is more likely than a gradual increase in the amount of adsorption up to the CMC.

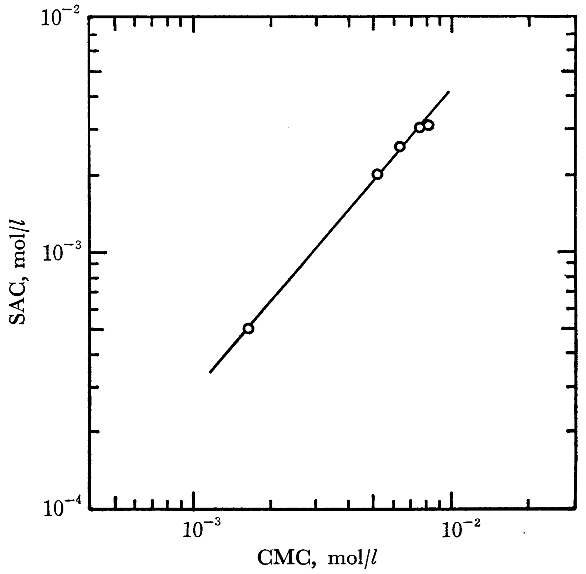

Fig. 5. Relation between SAC and CMC.

It is considered that, if the adsorbed phase can be assumed as a two-dimensional solution, the state of saturated adsorption at the surface may be considered as the formation of a two-dimensional micelle or a surface micelle; therefore, SAC corresponds to the concentration of the surface micellization, as in a usual micellization in the bulk solution. This similarity leads to the consideration that the surface phenomena of the surfactant solution at the air-solution interface, *e.g.*, foaming, surface viscosity, surface tension lowering and so on, may be expected to show some characteristic behavior in the vicinity of the SAC. For instance, Miles and Ross[15] and Dreger *et al.*,[16] applying the "pour test" to many sodium alkylsulfates in a foam experiment, found that the foam height first increased with the concentration and then reached a constant value at a concentration which was about 40—50% lower than the CMC. Also, Burcik[17] found the same tendency for the original foam volume of a sodium laurate solution, produced by the pouring method. Thus, the values of SAC might be used as another measure of the surface activity of the surfactant solution, which in some cases directly parallels the surface phenomena at the air-solution interface.

The author wishes to express his hearty thanks to Professor T. Sasaki for this encouragement and guidance throughout the experiments. He is grateful also to Professor M. Muramatsu for his helpful discussions and advice.

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13) F. van Voorst Vader, *Trans. Faraday Soc.*, **56**, 1067 (1960).
14) H. Lange, *Kolloid-Z.*, **153**, 155 (1957).
15) G. D. Miles and J. Ross, *J. Phys. Chem.*, **48**, 280 (1944).
16) E. E. Dreger, C. L. Keim, G. D. Miles, L. Shedlovsky, and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).
17) J. E. Burcik, *J. Colloid Sci.*, **5**, 421 (1950).