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Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. I. Accurate Measurement of Adsorption of Tritiated Sodium Dodecylsulfate

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We carried out direct measurement of adsorbed amount at the air-solution interface to confirm the validity of the Gibbs adsorption equation by using radiochemically and surface chemically pure tritiated sodium dodecylsulfate (TSDS) and a sheet scintillation counter, which was developed for the purpose of counting β-rays of tritium in air. The adsorbed amount increased with increasing SDS concentration and showed the saturation values of 3.19×10^{-10} mol/cm^2 in the concentration region from 3.2×10^{-3} to 14.4×10^{-3} mol/1000 g solution at 25°C. For the salt-free solution of ionic surfactant the Gibbs adsorption equation is confirmed to be valid for $n=2$ when activity in place of concentration is used. The equation of state for the ionic adsorbed film is further proposed. The cohesive pressure due to the attraction between hydrocarbon chains was given as a function of inverse molecular area.

The direct measurement of adsorbed amount, Γ, at the air-solution interface of ionic surfactant has been carried out by many workers to check the validity of the Gibbs adsorption equation.[1-4] Although a factor of $n=2$ in the Gibbs equation,[5] $d\gamma = -\boldsymbol{R}Tn\Gamma d \ln a$, is predicted theoretically, the experimental verification of the equation has

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[1] A. P. Brady, *J. Phys. Chem.*, **53**, 56 (1949); D. J. Salley, A. J. Weith, Jr., A. A. Argyle and J. K. Dixon, *Proc. Roy. Soc.* (London), **A203**, 42 (1950); B. A. Pethica, *Trans. Faraday Soc.*, **50**, 413 (1954); E. G. Cockbain, *ibid.*, **50**, 875 (1954); J. W. James and B. A. Pethica, "Proc. Intern. Congr. Surface Activity, 3rd," London, 2, 227 (1961).

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not been conclusive; several workers[2,3,6] indicate $n=1$ for ionic surfactant in a salt-free solution.

It is well known that the radiotracer method[7] is particularly suited for the measurement of Γ in many respects compared with the others such as "moving bubble" method[8] or microtome method.[9] However, the adsorption experiments using surfactants labelled with ^{14}C or ^{35}S involve considerable uncertainty in the measurement of Γ of ^{35}S-labelled sodium dodecylsulfate,[4] for instance, because these isotopes are not soft enough. On the other hand, owing to the extremely soft β-rays, ^{3}H renders the measurement of Γ highly accurate.[10] However, in such reports[7,11,12] which are still limited in number, the measurement of surface radioactivity is made with a 2π windowless gas-flow counter using humidified propane gas, which inevitably produces undesirable adsorption at "hydrocarbon gas-solution" interface instead of air-solution interface.

In the present paper, a radiochemically and chemically pure sample of tritiated sodium dodecylsulfate (TSDS) was synthesized and accurate determination of Γ at "air-solution" interface was made by employing a sheet scintillation counter.

Experimental

Materials. Sodium dodecyl-2,3-^{3}H,^{3}H sulfate (TSDS) was prepared by the previous method[13] with slight modifications. *n*-dodecene-2,3-ol-1 was synthesized from decanal and diethyl malonate[14] and the product was tritiated to give *n*-dodecan-2,2-^{3}H,^{3}H-ol-1 (TDOH). The unsaturated alcohol was purified by preparative gas chromatography (Yanagimoto GCG-3DH) and subsequently tritiated with tritium gas (Radiochemical Centre, Amercham, England, ca. 0.8 cc at S.T.P. 98% ^{3}H). The tritiated alcohol thus obtained was subjected to simultaneous gaschromatography (Yanagimoto GCG-5DH) for the substance and radioactivity. The results proved to be chemically and radio chemically pure for the sample obtained. It was then sulfated by the usual method[15] to give TSDS, which contained a trace amount of unreacted TDOH. The product was purified seven times by isotopic mixing with non-radioactive dodecanol in ethanol solution, followed by extraction with ether to remove dodecanol and to lower the specific activity of TDOH.[13] The specific activity of TSDS obtained was 9.16 Ci/mol. The surface-chemical purity of TSDS was confirmed by the disappearence of minimum near the critical micelle concentration (CMC) in surface tension versus concentration curve.

Thus, special care should be taken for the purity of the substance used. In fact, we had found[16] that many radioactive impurities are produced in the originally pure tirtiated stearic acid of specific activity of about 10 Ci/mol, when it is kept standing for 6.5 years in solid state. In the present experiments, therefore, the purification by Soxhlet extraction was continued until just before the adsorption experiments.

Water was distilled three times after being refluxed overnight by adding sulfuric acid and potassium permanganate. Ammonium sulfate used for the substrate solution was twice recrystallized from water and an oily substance was removed by ethereal extraction.

Apparatus. The tritium radioactivity was measured by the sheet scintillation counter,[17] modified so as to count the radioactivity at air-solution interface as shown in Fig. 1. The effective area of scintillator sheet (a) was 37.50 cm^2, and the periphery of the sheet was masked to avoid the effects of corners and edges of trough and scintillator sheet upon the scintillae. The scintillator probe was placed on the horizontally supported plate (b), which was moved vertically by the gear (c) at the rate of 2 mm per revolution. The counting was made at the applied voltage of 1250 V and with a discrimination with from 5 V to infinity.

All experiments were carried out in nitrogen gas atmosphere contained in a dark glove box. The gas controlled to 25°C by passing through a copper tube

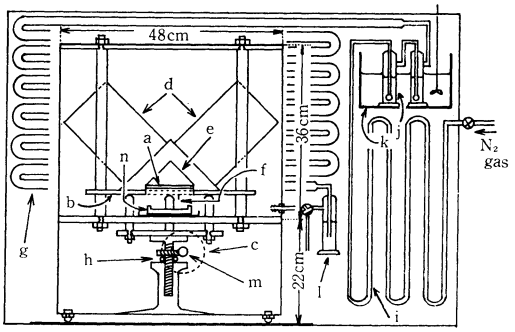

Fig. 1. Apparatus.

d: phototubes
e: prism
h: ball-bearing
k: water bath of 25°C
l: bubbler
For further details see text.

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(i) and completely humidified by passing through two bubblers (j) and a long tube (g) filled with pieces of wet paper was introduced in and allowed to leak slowly out of the cell to avoid the effects of carbon dioxide and evaporation on adsorption. Humidity of the gas was measured by the weight increase of $CaCl_2$ due to passage of the gas. It was found to be $98\pm3\%$ at 25.0 ± 0.2°C.

Procedure. An aqueous solution of TSDS was introduced into a Teflon trough (n in Fig. 1), and the surface of solution was carefully swept twice by a Teflon barrier. The end of the second sweeping was taken as time zero in the surface aging of adsorption. The scintillator probe was then lowered to a fixed position about 0.8 mm above the water surface, which was assured by the electric contact of Pt-electrode (f) fixed at the scintillator probe with aqueous solution connected to another electrode. The warm gear (m) and needle point electrode in Fig. 1 enabled the distance between the probe and the aqueous surface to be adjusted to within an accuracy of 0.02 mm. The standard deviation of counting rate due to this error was less than 1%. Counting was started to measure the time dependence of radioactivity over the surface of solution.

Results

Figure 2 shows the time dependence of radioactivity at the surfaces of SDS solution varying in its concentrations. The time required for attaining the saturation value of counting rate decreased with increasing bulk concentration of solution, and the time dependence practically disappeared above CMC.

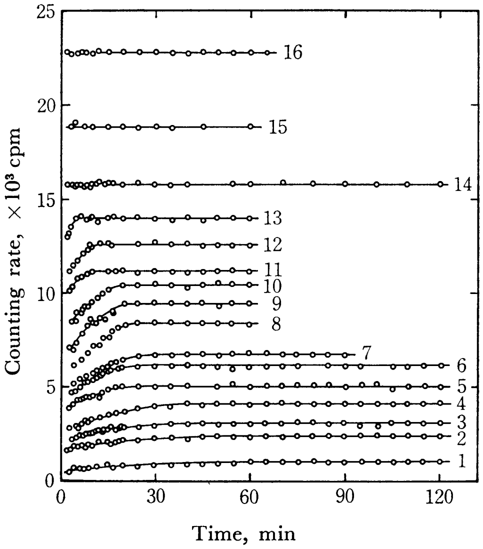

Fig. 2. Time dependence of total radioactivity on solution surface. Concentration of SDS (10^{-3} mol/1000 g solution)

1: 0.324	5: 2.02	9: 4.73	13: 8.05
2: 0.656	6: 2.47	10: 5.49	14: 9.29
3: 1.07	7: 3.04	11: 6.02	15: 11.33
4: 1.48	8: 4.09	12: 7.02	16: 14.38

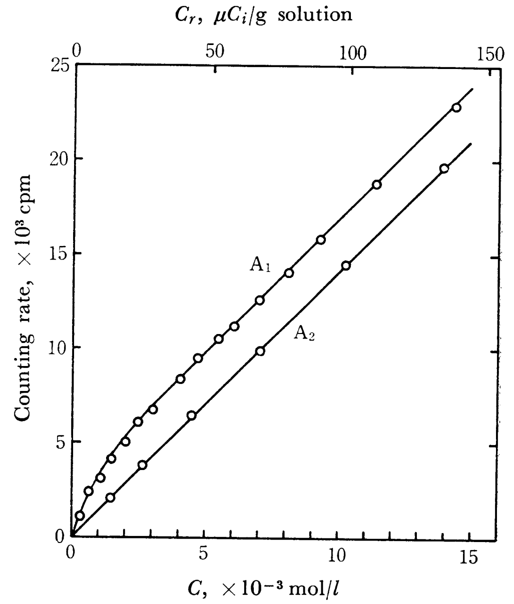

Fig. 3. A_1 plot for SDS and A_2 plot for DOH.

The counting rate of horizontal part in each curve of Fig. 2 was taken as the equilibrium value, A_1, which is plotted against SDS concentration in Fig. 3. The radioactivity due to the bulk of the solution, A_2, was determined from the radioactivity over the surfaces of the solutions of TDOH in non-radioactive DOH under the same geometrical conditions as that of A_1 determination. The A_2 values thus obtained were corrected for the difference in absorption and scattering of β-particles between water and DOH and plotted against radioactive concentration, C_r, in Fig. 3 in the same manner as in the previous report.[11] The calcu-

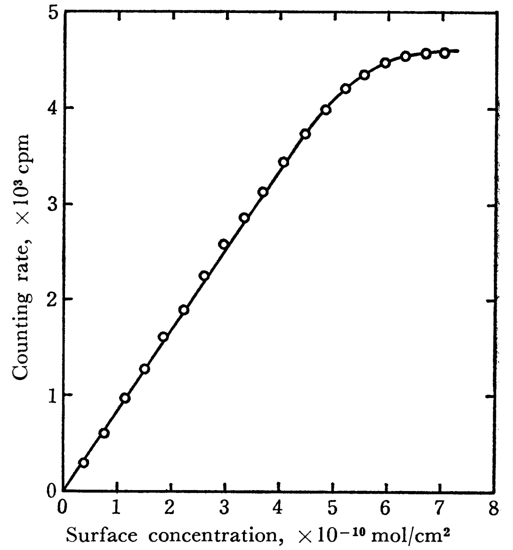

Fig. 4. Radioactivity *vs.* surface concentration for TSDS.

lation of Γ was made by

$$\Gamma = \frac{A_1 - A_2}{\kappa} \qquad (1)$$

where a constant κ must be known. It was determined by counting the surface radioactivity for known amounts of TSDS film spread over the aqueous ammonium sulfate solution of 80% saturation in the Teflon trough.[18] Figure 4 shows the relationship between the surface radioactivity and the amounts of TSDS.

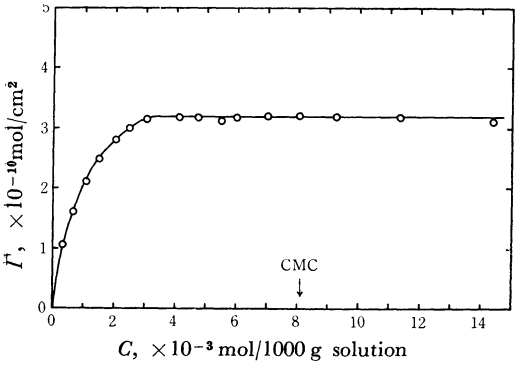

Fig. 5. Adsorption isotherm of SDS at air-solution interface (25°C).

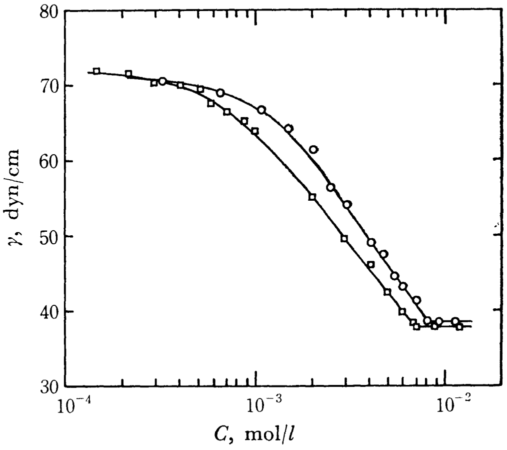

Fig. 6. Surface tension *vs.* concentration curves of SDS solution.

—○— : drop volume method
—□— : Wilhelmy plate method

The adsorption isotherm obtained is shown in Fig. 5. It can be seen that Γ markedly increases with increasing concentration of SDS and arrives at the saturated adsorption of 3.19×10^{-10} mol/cm^2 at bulk concentration of about 3.2×10^{-3} mol/1000 g solution beyond which Γ does not change

TABLE 1. ADSORBED AMOUNT AT GAS-SOLUTION INTERFACE OF SODIUM DODECYLSULFATE BY VARIOUS METHODS

Method	RI species	Saturated adsorption amounts, $\times 10^{-10}$ mol/cm^2	Temp. °C	Reference
RT	^{3}H	3.19	25	present paper
RT	^{3}H	5.0	25	3
RT	^{3}H	5.89	20	11
RT	^{35}S	3.7±1	28	4
RT	^{35}S	3.35		20
RT	^{35}S	7.5		21
RT	^{35}S	4.8±1		22
bubble		4.06	24—26	23
bubble		3.32	26	24
bubble		3.00	20	25
bubble		4.00	25	26
bubble		4.88	28	27
microtome		5.4	21—22	9*

* Sodium dodecylsulfonate

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with the concentration even beyond CMC (8.1×10^{-3} mol/1000 g solution). The area per molecule at the saturated adsorption is found to be 52.0 Å^2. The surface tension of the solution was measured by the drop volume method, the correction of Harkins and Brown being applied. The results (circles) shown in Fig. 6 show that the surfactant employed was surface-chemically pure. The Wilhelmy plate method was also adopted for the surface tension measurement for comparison.

Discussion

Evaluation of Γ. In Table 1 are shown the values obtained together with those obtained by other methods. The values are seen to fluctuate widely. Evidently the β-rays of ^{35}S are too hard for an accurate measurement of the SDS adsorption to be made, while ^{3}H much reduces the experimental error. However, the measurements of ^{3}H radioactivity with a 2π windowless gas-flow counter involve many difficulties which should be overcome. First, there is the possibility that the counting gas (humidified hydrocarbon) is adsorbed at the surface and solubilized in the bulk of surfactant solution.[19] Also, it is probable that the adsorption of the surfactant is affected by the high voltage applied and by the gas phase being hydrocarbon instead of air. These effects are unfavorable for the use of a 2π windowless gas-flow counter and the use of an end-window type is recomended.

It is seen in Table 1 that the results obtained happen to be close to some of the adsorption data obtained by the foam method. However, the latter method is not favorable because of the difference in adsorption on plane and non-plane surfaces, and also the difference in adsorption on solution surface and on two sided film where the van der Waals and coulombic interactions between the two parallel films are effective.[28] Difficulties also arise from uncertainty in the estimation of surface area, non-equilibrium state of adsorption due to the short period of passage of bubbles, and the gradual changes of bulk concentration and pH of solution during the passage of a large number of bubbles.[29] Thus, it is not surprising to find discrepancies in Γ values between the foam and the radiotracer methods, the latter being free of the difficulties mentioned above.

Surface Tension *vs.* Concentration Curve. Figure 6 shows the values of equilibrium surface tension, γ, measured by the Wilhelmy plate method[30] (squares) and by the drop volume method (circles) as a function of SDS concentration. A systematic difference seems to exist between surface tension data obtained by these methods. A similar tendency has been reported by Boucher *et al.*[31] for sodium hexyl α-sulfopelargonate. They inferred that the surface tension data obtained by these methods appear to be reliable in so far as they do not affect molecular cross-sectional areas of surfactants obtained by applying these data to the Gibbs equation. However, the results of the present measurement exhibited limiting slopes of curves being different from each other as shown in Fig. 6. This would be reasonable, when we consider marked aging phenomena observed in surface tension of detergent solution.

Gibbs Adsorption Equation. In the present system the Gibbs adsorption equation[5] is expressed by

$$-\mathrm{d}\gamma = \boldsymbol{R}T\Gamma_{\mathrm{Na}^+}\mathrm{dln}a_{\mathrm{Na}^+} + \boldsymbol{R}T\Gamma_{\mathrm{D}^-}\mathrm{dln}a_{\mathrm{D}^-} + \boldsymbol{R}T\Gamma_{\mathrm{H}^+}\mathrm{dln}a_{\mathrm{H}^+} + \boldsymbol{R}T\Gamma_{\mathrm{OH}^-}\mathrm{dln}a_{\mathrm{OH}^-} \qquad (2)$$

where γ, Γ and a express the surface tension of solution, the amount of adsorption and activity, both for the solutes. The subscripts Na$^+$, D$^-$, H$^+$, and OH$^-$ denote sodium, dodecylsulfate, hydrogen and hydroxyl ions, respectively. Since the SDS solution was almost neutral and pH was kept practically constant to 6.0±0.2 throughout the measurements for all solution, we put for approximation $\mathrm{d}\,a_{\mathrm{H}^+}=\mathrm{d}\,a_{\mathrm{OH}^-}=0$. Assuming no surface hydrolysis,[32] $\Gamma_{\mathrm{H}^+}=\Gamma_{\mathrm{OH}^-}=0$, and electrical neutrality both in bulk and surface layer, namely $C_{\mathrm{Na}^+}=C_{\mathrm{D}^-}=C$, and $\Gamma_{\mathrm{Na}^+}=\Gamma_{\mathrm{D}^-}=\Gamma$,[33] we get from Eq. (2)

$$-\frac{\mathrm{d}\gamma}{\boldsymbol{R}T\,\mathrm{d}\ln C} = 2\Gamma\left(1+\frac{\mathrm{d}\ln f_\pm}{\mathrm{d}\ln C}\right) \qquad (3)$$

where $f_\pm=(f_{\mathrm{Na}^+}\times f_{\mathrm{D}^-})^{1/2}$ is the mean activity coefficient of SDS. It has been reported[34] that activity coefficient of SDS solution varies according to the method of measurement such as the glass or membrane electrode methods. However, $f_\pm$ is better approximated by the Debye-Hückel second approximation. Thus, for uni-univalent

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electrolytes, we have

$$-\ln f_{\pm} = \frac{1.18\sqrt{C}}{1+\frac{r_{\pm}}{3.08}\sqrt{C}} \tag{4}$$

where $r_{\pm}$ is the average radius of hydrated anion and cation in the solution (Å unit). According to Kielland's report[35] and in agreement with Haydon's opinion[36] that $r_{\pm}$ for alkylsulfate and quaternary ammonium ions should be slightly higher than 5 Å, we put $r_{\pm}=7$ Å in Eq. (4) for SDS ion of all concentration. Differentiating Eq. (4) we have

$$\Delta = -\frac{\mathrm{d}\ln f_{\pm}}{\mathrm{d}\ln C} = \frac{0.59\sqrt{C}}{\left(1+\frac{r_{\pm}}{3.08}\sqrt{C}\right)^2} \tag{5}$$

The values of Γ were calculated from Eq. (3) by the evaluation of $\mathrm{d}\gamma/\mathrm{d}\ln C$ from γ *vs.* C measurement and Δ from Eq. (5). The result is shown in Fig. 7 as solid and broken lines for the Wilhelmy plate and the drop volume methods, respectively. The amount of adsorption directly measured by the radiotracer method was also plotted as shown by circles in Fig. 7. The observed values are in good agreement with those calculated by Eq. (3) applying the surface tension data of the Wilhelmy plate method, compared with those of drop volume method throughout the whole range of bulk concentration. The deviation of drop volume data is marked especially at low concentration. This may be understood since the drop volume method is insufficient for giving an equilibrium surface tension at low concentration where the rate of attainment of equilibrium is slow. On the other hand, a slight discrepancy at lower concentration in the case of the Wilhelmy plate method probably comes either from the uncertainty of surface tension data or from the invalidity of Eq. (3), which has been derived by neglecting the H+ ion terms.

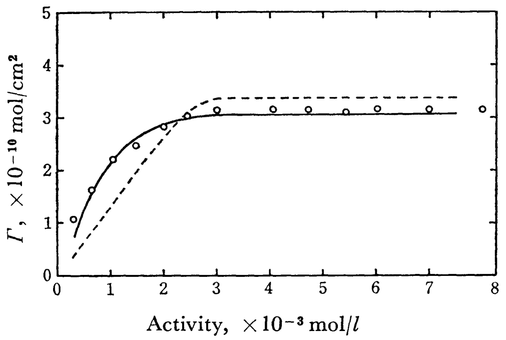

Fig. 7. Comparison of observed and calculated values of SDS adsorption using Eq. (3).

○ : observed values
··· : calculated values (drop volume method)
— : calculated values (Wilhelmy plate method)

It should be emphasized that for the salt-free solution of not so dilute ionic surfactant the Gibbs adsorption isotherm is proved to be valid for $n=2$ in the Gibbs adsorption equation, provided that activity is used in place of concentration.

Equation of State. Many investigators have reported[36,37] various types of equation of state for the monomolecular film at an air-solution interface. Davies proposed a surface equation of state,[38]

$$(\pi-\pi_s-\pi_r)(A-A_0) = \boldsymbol{k}T \tag{6}$$

for charged monolayer at air-water interface, where π is the total surface pressure, A and A_0 the area and co-area per molecule in adsorbed film, $\boldsymbol{k}$ the Boltzmann constant, T the absolute temperature, π_s the cohesive surface pressure due to the van der Waals forces of attraction between the hydrocarbon parts of the adsorbed surface-active ions as given by

$$\left.\begin{array}{l} \pi_s = -\dfrac{400\,m}{A^{3/2}} \\ \text{for } A>71\ \text{Å}^2\text{/molecule, and} \\ \pi_s = -0.67\,m \end{array}\right\} \tag{7}$$

for $A<71$ Å^2/molecule, with m for the effective number of CH$_2$ groups present in the long-chain ion. Further, π_r in Eq. (6) represents the repulsive surface pressure due to the polar head groups of adsorbed ions. Davies gave

$$\pi_r = 6.03C_i^{\frac{1}{2}} - \frac{2\boldsymbol{k}T}{A} \tag{8}$$

where C_i denotes total (uni-univalent) electrolyte concentration.

Figure 8 shows the observed equation of state for the adsorbed film of SDS, using the data of surface tension measured by the Wilhelmy plate method and the amount of adsorption by radiotracer method. In Fig. 9 plots of $1/(\pi-\pi_s-\pi_r)$ against A are shown as circles, assuming that π_s and π_r are expressed by Eqs. (7) and (8), respectively. If we draw a line with the slope of $\boldsymbol{k}T$ and through the point $A_0=33$ Å^2 given by Davies for adsorbed films of SDS, it largely deviates from the observed values (circles). This clearly shows the inapplicability of the empirical equation (7), which has been presumed from the behavior of π *vs.* A relation for the monolayer of octadecyltrimethylam-

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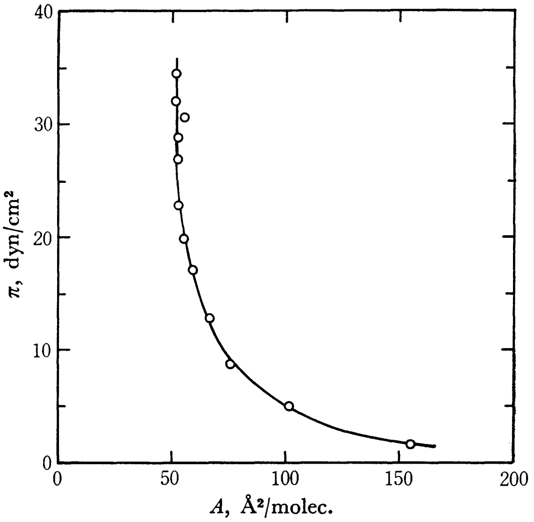

Fig. 8. Pressure *vs.* area curve of SDS at air-solution interface.

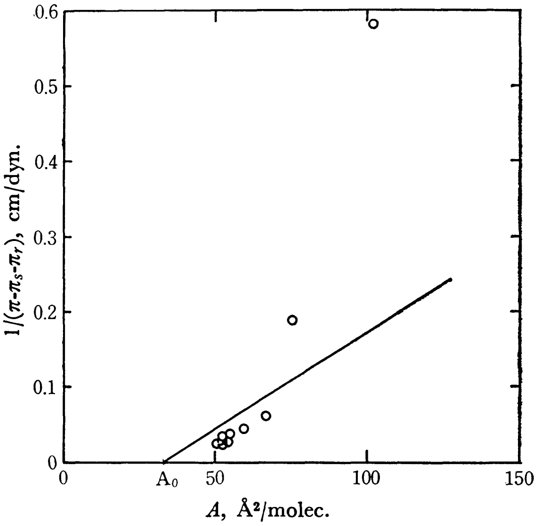

Fig. 9. Plots of $1/(\pi\text{-}\pi_s\text{-}\pi_r)$ against A for SDS.

○ : observed values
— : calculated from Davies equation

monium ions, but has not yet been confirmed actually, at least for monolayers of shorter carbon chain length. Thus, Eq. (7) turned out to be inapplicable to soluble adsorbed films, and the present authors propose the empirical equation

$$\pi_s = -\frac{K}{A} \tag{9}$$

where K is a proportionality constant, determined from the π *vs.* A curve. Substitution of Eqs. (8) and (9) into Eq. (6) yields an equation of rectangular hyperbola when $A(\pi-\pi_r)$ is plotted against A. Thus, graphical plots give

$$K = 2.43\,\boldsymbol{k}T$$

$$A_0 = 38.4\,\text{Å}^2/\text{molecule}$$

and the final equation becomes

$$\left(\pi+6.03\,C_i^{\frac{1}{2}}+\frac{0.43\,\boldsymbol{k}T}{A}\right)(A-A_0) = \boldsymbol{k}T \tag{10}$$

Figure 10 shows the curves based on Davies' equation and Eq. (10) together with the experimental data (circles). Eq. (10) is shown to fit the actual behavior of adsorbed film better than Davies' equation. The observed π *vs.* A curve shows a more condensed film than that predicted by Davies' equation. The large deviation of Davies' equation, especially in the region of large molecular area, may be ascribed to the insufficient contribution of π given by Eq. (7) to total surface pressure. It should be emphasized that Eq. (10) holds regardless of the value of A being smaller or larger than 71 Å²/molecule, which is not the case in Eq. (7). It is shown that Eq. (10) with $K=2\boldsymbol{k}T$ and $A_0=27.0$ Å²/molec. also fits the π *vs.* A curve for the monolayer of octadecyltrimethylammonium ion, while Davies' equation fairly deviates from the curve.

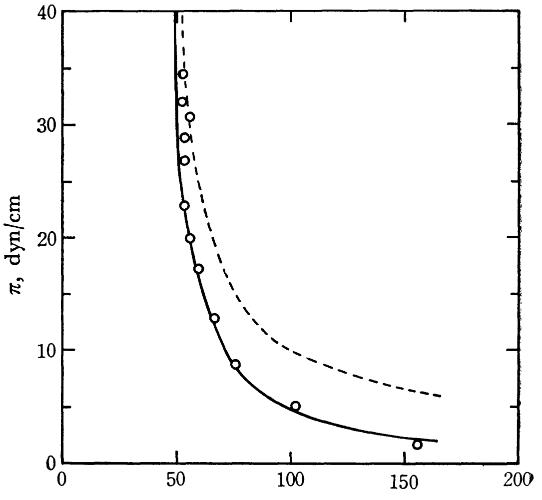

Fig. 10. π *vs.* A plot for SDS.

○ : observed values
— : Eq. (10)
··· : Davies equation

Recently, Chattoraj *et al.*[39] proposed the following equation for π_s on the basis of the two-dimentional van der Waals attraction,

$$\pi_s = \frac{\alpha_s}{A^2} \tag{11}$$

where α_s is the van der Waals constant for a surface phase. To explain the deviation of Eq. (11)

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[39] C. K. Chattoraj and A. K. Chatterjee, *J. Colloid Interfac. Sci.*, **21**, 159 (1966).

from their experimental data, they assumed the existence of surface micelles for the region of $A<130$ Å^2/molecule. In the present studies, however, Eq. (11) has been confirmed not to hold in the region of $A<150$ Å^2/molecule, suggesting the inapplicability of their equation and the uncertainty of the existence of surface micelles in adsorbed layer.

As for the value of A_0 for the charged adsorbed films, there is always disagreement among various authors. Phillips and Rideal[40] give $A_0=20$ Å^2 for the dodecylsulfate ion, and Davies[38] considers 33 Å^2 reasonable, though Cook and Tablot[41] suggest A_0 being as large as 50 Å^2. The present experiments give $A_0=38.4$ Å^2. This value is reasonable when we take account of the fact that the cross-sectional area for a hydrated sulfate ion is 28 Å^2 per molecule.[42] The difference may be ascribed to the presence of the hydrocarbon chain attached to the ion. It should be emphasized that the value A_0 obtained in the present study is based upon the equation of state which is in agreement with the direct measurement of π *vs.* A relation, while the values of other workers are based upon the equations which are not in agreement with the experimental results, at least for SDS.

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[40] J. N. Phillips and E. Rideal, *Proc. Roy. Soc.*, **A232**, 159 (1955).

[41] M. A. Cook and E. L. Tablot, *J. Phys. Chem.*, **56**, 412 (1952).

[42] R. D. Vold and M. J. Vold, Ed., "Colloid Chemistry," Reinhold Pub. Corp., N. Y. (1964), p. 100.