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Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. II. The Effect of Excess Salt on the Adsorption of Sodium Dodecylsulfate

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The adsorbed amount and the surface tension at the air-solution interface of the solution of tritiated sodium dodecylsulfate in the presence of excess common inorganic salt have been accurately measured at 25°C. The radioactivity of tritium β-rays over the solution was counted with a sheet scintillation counter and the surface tension of the solution was measured by a drop volume method. In the sodium dodecylsulfate solution containing sodium chloride of 0.115 mol/*l*, the adsorbed amount of dodecylsulfate ions was saturated to give 4.33×10^{-10} mol/cm^2 when the bulk concentration was higher than 5.0×10^{-4} mol/1000 g solution. In the presence of the excess inorganic salt common to the ionic surfactant in solution the Gibbs adsorption isotherm has been experimentally proved to be valid for $n=1$. Moreover, it was confirmed that the equation of state for the ionic adsorbed film on the salt-free solution proposed previously is also applicable to the ionic surfactant solution with the excess salt.

The behavior of the surface active substances at the air-solution interface has been studied by many investigators. In spite of the vast amount of studies published up to the present, there are few papers[1-3] which discuss the validity of the Gibbs adsorption isotherm on the basis of reliable data directly obtained for the system of surfactant solution with or without the addition of salt.

In the preceding paper,[4] the adsorbed amount at the air-solution interface was accurately measured by means of a radiotracer method by using the aqueous solution of tritiated sodium dodecylsulfate (TSDS). It was experimentally confirmed for TSDS solution in the absence of added inorganic salt that, if the activity coefficient is taken into account, the adsorption of detergent ions at the air-solution interface takes place in accordance with the Gibbs adsorption isotherm applied for the aqueous binary strong electrolyte solution.

In the present study, the adsorption experiments have been extended to the aqueous solution of TSDS in the presence of excess common inorganic electrolyte. The surface tension of the solution has been measured to check the Gibbs adsorption isotherm and to confirm the equation of state of adsorbed film established in the preceding paper.[4]

Experimental

Materials. The radioactive SDS was synthesized and purified as described in the preceding papers.[4,5] Its specific activity was 12.0 Ci/mol. Sodium chloride used as an inorganic salt was of extra pure grade, which was further purified by recrystallization from the saturated solution by passing HCl gas, by roasting, and then

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[1] C. P. Roe and P. D. Brass, *J. Amer. Chem. Soc.*, **76**, 4703 (1954).

[2] G. Nilsson, *J. Phys. Chem.*, **61**, 1135 (1957).

[3] R. Matuura, H. Kimizuka and K. Yatsunami, This Bulletin, **32**, 646 (1959).

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

[5] M. Muramatsu and K. Tajima, *J. Labelled Compounds*, **2**, 304 (1966).

by ethereal Soxhlet extraction. Such purification was repeated until surface tension of the salt solution reached the constant value. Water used in these experiments was triply distilled. For the preparation of the solution, TSDS was dissolved in the aqueous solution of sodium chloride of constant concentration (0.115 mol/*l*).

Method. The measurements were made in a glove box with nitrogen atmosphere, which was kept at 98±3% humidity and 25±0.2°C. The procedure used for the measurement of the adsorption of TSDS was the same as described in detail in the preceding papers.[4,6] The surface radioactivity was measured by a sheet scintillation counter.

The surface tension measurement was carried out with another portion of the solution used for the adsorption experiment. The drop volume method was adopted with applying the Harkins and Brown corrections.[7] The equilibrium drop volume was obtained within 5 min. The calculation of surface tension was made with the mean volume of 5—10 drops at least. Throughout all experiments, the pH of bulk solutions was controlled at 6±0.2.

Results and Discussion

Figure 1 shows the time dependence of the total surface radioactivity over the solution, A_1, for TSDS solutions of varying concentrations. It was found that the rate of adsorption of dodecylsulfate ion was far greater than the rate of adsorption of salt-free solution, and that time dependence of A_1 did not appear even at concentration below the critical micelle concentration (CMC), except the case of very low TSDS concentration. These phenomena are qualitatively in agreement with the observation on the time dependence in surface tension lowering of the surfactant solution.[8] A_1 value at equilibrium adsorption was obtained as the steady counting rate of each curve in Fig. 1, and given in Fig. 2 as a function of SDS concentration. By subtracting the radioactivity, A_2, due to the bulk of the solution from A_1, surface radioactivity, was obtained and it was converted to surface excess, Γ, by multiplying the conversion factor in the same manner as in the preceding paper.[4]

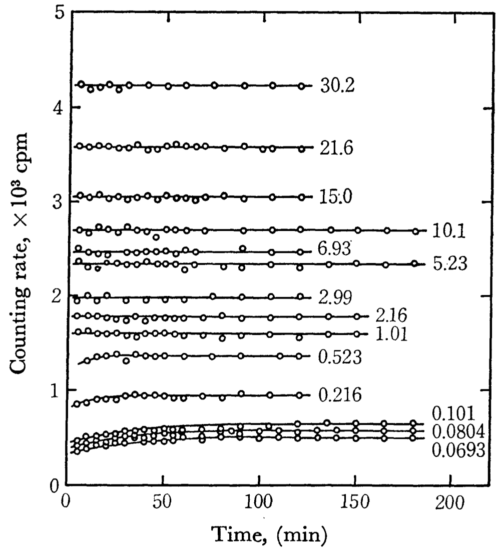

Fig. 1. Time dependence of total radioactivity at solution surface. Figures denote concentration of TSDS in bulk solution, in 10^{-4} mol/1000 g solution.

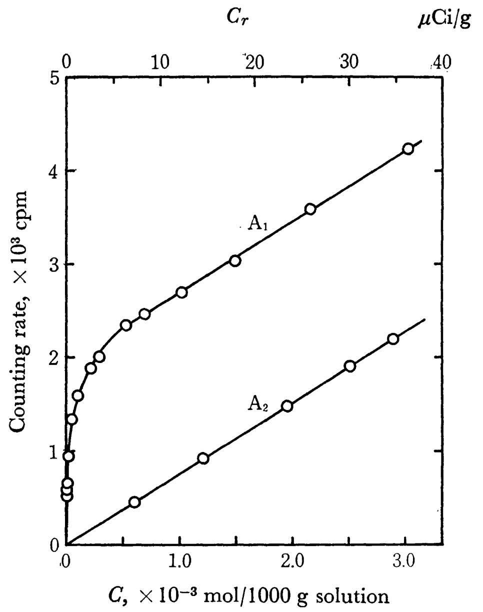

Fig. 2. A_1 and A_2 as a function of concentration of TSDS, C, and radioactive concentration, C_r, respectively.

Figure 3 shows the adsorption isotherm thus obtained at the air-solution interface of the TSDS solution containing excess sodium chloride. The

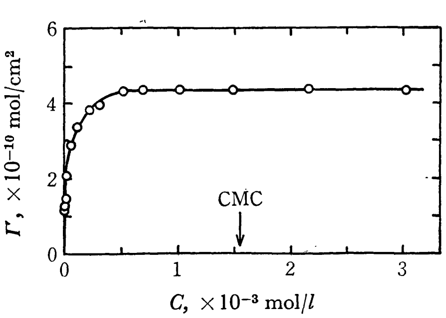

Fig. 3. Adsorption isotherm of TSDS solution in the presence of excess common inorganic electrolyte (25°C).

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6) M. Muramatsu, K. Tajima and T. Sasaki, This Bulletin, **41**, 1279 (1968).

7) W. D. Harkins and F. E. Brown, *J. Amer. Chem. Soc.*, **41**, 499 (1919).

8) N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938); G. C. Nutting, F. A. Long and W. D. Harkins, *J. Amer. Chem. Soc.*, **62**, 1946 (1940).

adsorbed amount increases rapidly with increasing bulk concentration and to attain the value of saturated adsorption (4.33×10^{-10} mol/cm^2) when the bulk concentration was higher than 5.0×10^{-4} mol/1000 g solution. The saturated adsorption was kept constant even above the CMC within the limit of error. The apparent area per surfactant molecule at saturated adsorption is 38.4 Å^2, while the corresponding value for salt-free solution is 52.0 Å^2 as reported in the previous paper.[4]

Nilsson reported[2] that, in a buffer solution of $\text{pH} = 6.5$ and of sodium ion concentration $C_{\text{Na}^+} = 0.1$ mol/l, the amount of adsorption increases gradually with increasing bulk concentration up to CMC and becomes constant above the CMC, the saturated adsorption of dodecylsulfate ion being nearly 5.3×10^{-10} mol/cm^2 at 25°C. Matuura *et al.*[3] also measured adsorption at the air-solution interface of ^{35}S-labelled SDS containing 0.1 mol/l NaCl, and showed a similar increase in adsorption up to CMC, the adsorbed amounts being somewhat lower than those by Nilsson. The present result does not agree with these results except for the occasional agreement in a region of low SDS concentration.

As to the disagreement of the adsorption isotherms among various investigators, it is pointed out that a 2π windowless gas-flow counter, which Nilsson adopted to measure the adsorption amount, gives much unavoidable influence on the adsorption as described in detail in the previous report.[4] The value obtained by such a method might generally be higher than that of the counter of end-window type. On the other hand, higher accuracy may be expected for the present result than for Matuura's at high SDS concentration, since the radiation from ^{3}H is far softer than ^{35}S. Thus, the results of the present experiment are considered to be most reliable among them.

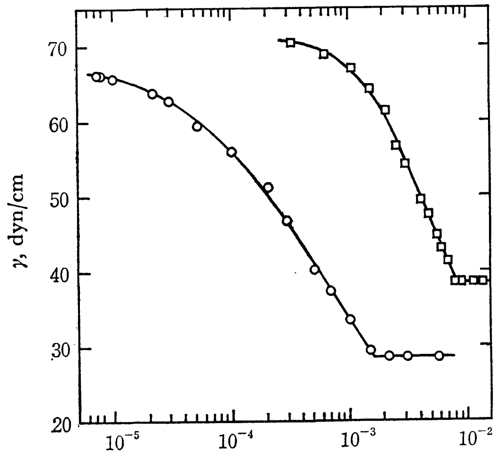

Fig. 4. Surface tension *vs.* concentration of TSDS solution.

—□—: salt-free solution

—○—: excess salt solution

Figure 4 shows the curve of the surface tension *vs.* concentration obtained under the same experimental conditions as reported in the preceding paper.[4] It is noted from Fig. 4 that a constant slope is obtained in the range of TSDS concentration from about 5.0×10^{-4} mol/l to the CMC.

Gibbs Adsorption Isotherm. The Gibbs adsorption isotherm is expressed as follows:

$$-\,\mathrm{d}\gamma = \boldsymbol{RT}\sum \Gamma_i \,\mathrm{d}\ln a_i \qquad (1)$$

where γ represents the surface tension, Γ_i and a_i, the surface excess and the activity of ith ionic species in the solution, respectively. Assuming that the bulk solution is neutral and surface hydrolysis is absent (bulk pH was confirmed to be constant, independently of the TSDS concentration), Eq. (1) is rewritten for the TSDS solution containing sodium chloride as,

$$-\,\mathrm{d}\gamma = \boldsymbol{RT}\Gamma_{\text{Na}^+}\,\mathrm{d}\ln a_{\text{Na}^+} + \boldsymbol{RT}\Gamma_{\text{D}^-}\,\mathrm{d}\ln a_{\text{D}^-} + \boldsymbol{RT}\Gamma_{\text{Cl}^-}\,\mathrm{d}\ln a_{\text{Cl}^-} \qquad (2)$$

where the subscripts Na$^+$, D$^-$ and Cl$^-$ denote sodium, dodecylsulfate and chloride ions, respectively. In the case of excess and constant concentration of NaCl, we have,

$$\frac{\mathrm{d}C_{\text{Cl}^-}}{\mathrm{d}C_{\text{D}^-}} = 0, \text{ and } \frac{\mathrm{d}C_{\text{Na}^+}}{\mathrm{d}C_{\text{D}^-}} \simeq 0 \qquad (3)$$

From Eq. (3) and the mean activity coefficient $f_\pm$, Eq. (2) can be written as,

$$-\frac{\mathrm{d}\gamma}{\boldsymbol{RT}\,\mathrm{d}\ln C_{\text{D}^-}} = \Gamma_{D^-} + 2(\Gamma_{D^-} + \Gamma_{\text{Cl}^-})\frac{\mathrm{d}\ln f_\pm}{\mathrm{d}\ln C_{\text{D}^-}} \qquad (4)$$

The differential term in the right side of Eq. (4) can be evaluated as,

$$2 \times \frac{\mathrm{d}\ln f_\pm}{\mathrm{d}\ln C_{\text{D}^-}} = 1.17\frac{C_{\text{D}^-}}{C_{\text{Na}^+}{}^{1/2}} = 5.27 \times 10^{-3} \qquad (5)$$

for $C_{NaCl} = 0.115$ mol/l and $C_{D^-} = \text{CMC}$, with the assumption of the Debye-Hückel limiting law to be held. Thus, the differential term in Eq. (4) is seen to be negligible in this case. Then, Eq. (4) is reduced to

$$\Gamma = -\frac{\mathrm{d}\gamma}{\boldsymbol{RT}\,\mathrm{d}\ln C} \qquad (6)$$

where C is the concentration of the surfactant and is taken to be equal to C_{D^-}, and $\Gamma = \Gamma_{D^-}$. The values of Γ calculated by Eq. (6) from the data of surface tension in Fig. 4 are plotted against SDS concentration in Fig. 5 together with the observed values for comparison. The calculated values are in good agreement with the observed values throughout the whole range of bulk concentration studied. When the surface attains the saturation with adsorbed surfactant at the concentration of 5.0×10^{-4}

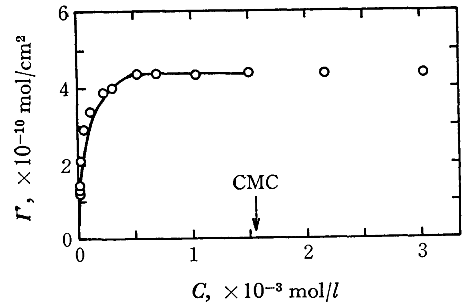

Fig. 5. Adsorption isotherm of SDS solution.
○: observed value
———: Eq. (6)

mol/l as shown in this figure, further increase of the bulk surfactant concentration produces no change in the amount of adsorption, while it causes a steady decrease of surface tension. Such a mode of adsorption isotherm was confirmed to persist even above the CMC. Roe and Brass[1] measured the surfate tension lowering of SDS solution of which pH and C_{Na^+} were held constant to 6.5 and 0.1 mol/l, respectively, by the use of the buffer solution, and calculated the amount of SDS adsorption by applying the Gibbs equation. They obtained 4.40×10^{-10} mol/cm^2 as the values of saturated adsorption. This value is also in good agreement with that measured in the present radiotracer study as far the saturation value is concerned.

Thus, the Gibbs adsorption isotherm is proved to be valid, when we put $n=1$ in the Gibbs equation[4] for TSDS solution in the presence of excess salt with the common cation.

Equation of State. The relation between the surface pressure, π, and molecular area, A, of the adsorbed film of TSDS on an excess salt solution was calculated from the data of Figs. 3 and 4 by using the following relationships:

$$\pi = \gamma_0 - \gamma$$

$$A = \frac{1}{\Gamma_{\mathrm{D}^-} \times N}$$

where γ_0 is the surface tension of water and N Avogadro's number. The result is shown by circles in Fig. 6. In the preceding report[4] we proposed the equation of state for the adsorbed film on the salt-free SDS solution as follows:

$$\left(\pi + \frac{0.43\,kT}{A} + 6.03\,C_i^{1/2}\right)(A - A_0) = kT \qquad (7)$$

where C_i is the total bulk concentration of ions, A_0 the coarea per molecule, k the Boltzmann constant and T the absolute temperature. In Fig. 6, Eq. (7) is shown by a solid line. An excellent agreement is seen between Eq. (7) and the experimental results. The value of A_0 was found to be about 25.0 Å^2/molecule, which was obtained by the same procedure as that in the preceding paper.[4] This value may be compared with the value of $A_0=38.4$ Å^2/molecule found in the case of salt-free solution. The effects of added salt on A_0 may be interpreted as being due to the shrinkage of diffuse double layers and the dehydration of adsorbed dodecylsulfate ion.

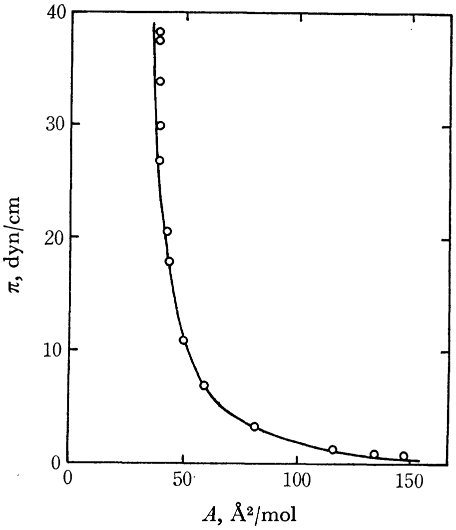

Fig. 6. π *vs.* A plot for adsorbed SDS monolayer on 0.115 mol/l NaCl solution at 25°C.
○ : observed value
———: Eq. (7)

It is confimed from Fig. 6 that Eq. (7) expresses satisfactorily behavior of the surface films adsorbed from ionic surfactant solutions with or without excess salts.

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