The Study of the Adsorption of Detergents at a Solution-Air Interface by Radiotracer Method. III. The Effect of Inorganic Electrolytes on the Adsorption of Sodium Dodecyl Sulfate

By Ryohei MATUURA, Hideo KIMIZUKA and Katsumasa YATSUNAMI

(Received November 17, 1958)

Roe and Brass[1], Nilsson[2] and Salley et al.[3] have checked the Gibbs adsorption equation with potassium palmitate, sodium dodecyl sulfate and Aerosol OTN in the presence of potassium hydroxide, sodium chloride and Aerosol OT, respectively. They have obtained the result that the adsorption of detergent at the air-solution interface takes place in accordance with the Gibbs adsorption equation. It was suggested also through the observation of the change with time in surface tension of detergent solution that the addition of excess electrolytes increases the adsorption rate of surface active ion[4].

However, the adsorption isotherm and adsorption rate for the detergent solution in the presence of various electrolytes, especially in the presence of the salts containing no common ion with the detergent, has not yet been measured directly. In the present study, we have succeeded by the aid of the radiotracer method in measuring directly the adsorption of dodecyl sulfate ion (abbreviated as DS^-) at the solution-air interface from the solutions containing sodium dodecyl sulfate (abbreviated as SDS) and excess inorganic electrolytes. The surface tension of the solution has been measured and the Gibbs adsorption equation has been checked.

Experimental

Materials. — The radioactive SDS used was synthesized as described in the preceding paper[5]. Of the inorganic electrolytes, manganous and aluminum chlorides were those of extra pure reagents and purified by recrystallization, while sodium, potassium and magnesium chlorides were those of guaranteed reagents and used without further purification. For the preparation of the solution under investigation, SDS was dissolved in the aqueous solution of respective inorganic electrolyte with a given concentration.

Method.—The procedure used for the measurement of the surface excess of DS^- was the same as described in the preceding paper[5,6]. The surface count of radioactive sodium sulfate solution was taken as the same as that of the bulk of radioactive SDS solution, both containing excess of salts.

The surface tension measurement was carried out by means of the du Noüy tensiometer. The temperature of the experiment was maintained at 29±1°C.

Results and Discussion

It was found that the adsorption of DS^- in the presence of excess salts with or without common ions was so rapid that

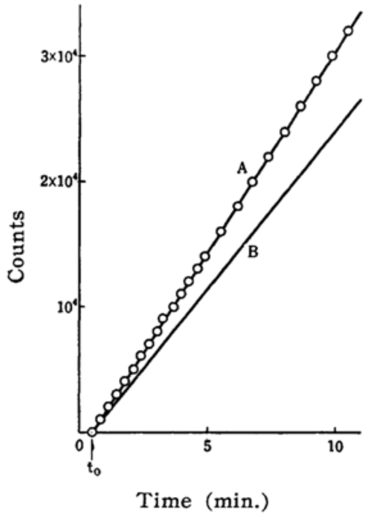

Fig. 1. Count vs. time relation for the solution A containing 5.543×10^{-4} mol./l. SDS and 0.3 N NaCl and the solution B containing 5.543×10^{-4} mol./l. Na_2SO_4 and 0.3 N NaCl, 29±1°C.

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[3] H. Sobotka, "Monomolecular Layers", The American Association for Advancement of Science, Washington, D. C. (1954), p. 81.

[4] N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938); K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939); G. C. Nutting, F. A. Long and W. D. Harkins, *J. Am. Chem. Soc.*, **62**, 1946 (1940).

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

[6] R. Matuura, H. Kimizuka, S. Miyamoto, R. Shimozawa and K. Yatsunami, ibid., **32**, 404 (1959).

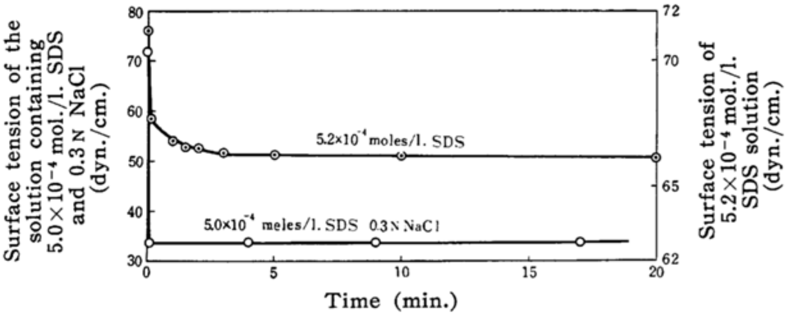

Fig. 2. Effect of the presence of sodium chloride on the surface tension of SDS solution, 29±1°C.

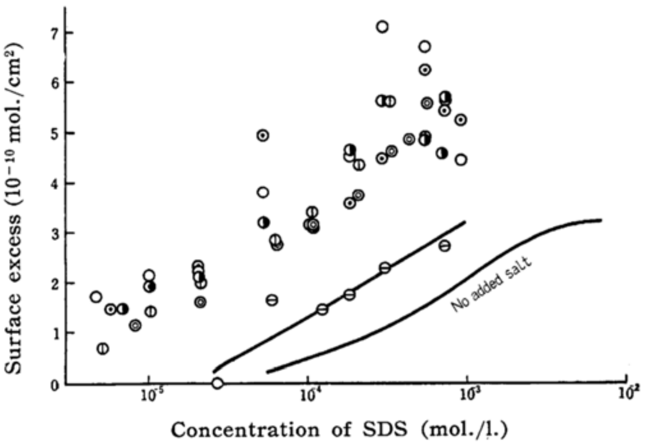

Fig. 3. Effect of addition of sodium chloride on the adsorption of DS^-, 29±1°C. ⊖ 0.01 N NaCl, ◎ 0.1 N NaCl, ⦶ 0.2 N NaCl, ◑ 0.3 N NaCl, ⊙ 0.5 N NaCl, ○ 1.0 N NaCl.

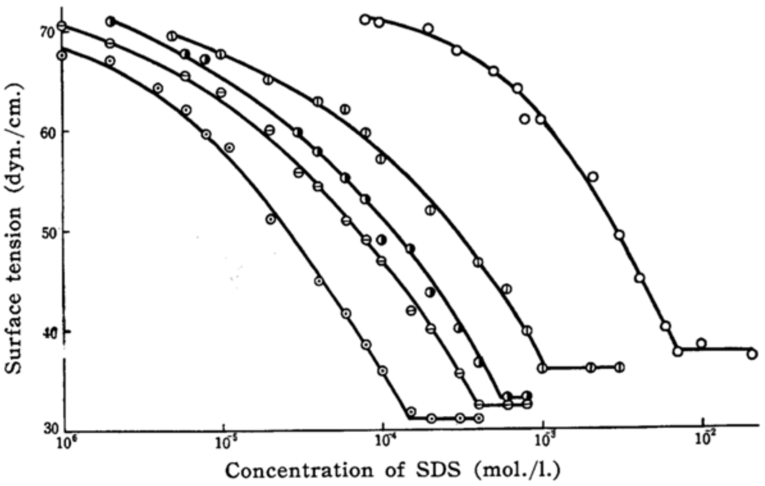

Fig. 4. Effect of added sodium chloride on the surface tension of SDS solution, 29±1°C. Numericals in this figure show the concentration of sodium chloride in N.

○ no added NaCl, ⦶ 0.1 N NaCl, ◑ 0.3 N NaCl, ⊖ 0.5 N NaCl, ⊙ 1.0 N NaCl.

the equilibrium was attained within one minute, while without added salts it took several minutes or more to reach the adsorption equilibrium at the solution-air interface as was reported in the preceding paper⁶⁾. Fig. 1 is an example of counts vs. time relation of SDS solution (concentration is 5.543×10^{-4} mol./l.) containing 0.3 N sodium chloride. t_0 in Fig. 1 is the starting time of counting. It is seen that a linear relation is held between count and time, showing that the adsorption has already reached equilibrium at the starting time (t_0) of counting. It has already been known that the presence of inorganic salts makes faster the attainment of equilibrium of surface tension of the detergent solution⁴⁾. In the present study, the effect of the presence of sodium chloride on the change with time of surface tension of SDS solution was also measured by means of the Wilhelmy plate method. Fig. 2 shows an example of the effect of the presence of sodium chloride on the rate of surface tension lowering. It may easily be seen that the presence of salt not only makes faster the attainment of equilibrium of surface tenstion, but also lowers the surface tension value. Furthermore, it may be pointed out that in the presence of salt the surface tension almost reaches equilibrium even at the starting time of experiment. The present experiment, therefore, clearly shows that the rapid rate of surface tension lowering actually corresponds, as might be expected, to the rapid rate of adsorption at least qualitatively. However the rate of adsorption was too rapid to measure precisely and so the quantitative relation between the surface tension lowering and the adsorption before reaching equilibrium could not be determined in the present study. The results and discussions below therefore are concerned only with the equilibrium state of adsorption and surface tension.

First the effect of sodium chloride of various concentrations on the adsorption of DS⁻ was measured and the result is shown in Fig. 3. It is obvious that the presence of excess sodium chloride increases the adsorption of DS⁻ considerably. Here it is to be noted that, although below 0.1 N of sodium chloride the adsorption of DS⁻ increases with the concentration of the salt, above 0.1 N of sodium chloride the values of surface excess of DS⁻ fall within a range almost independent of the concentration of the salt. On the contrary, the surface tension of SDS solution containing sodium chloride decreases regularly with the concentration of the salt up to 1 N, as shown in Fig. 4.

When the Gibbs adsorption equation for the solution of surface active electrolyte is written in the form

$$\Gamma = -\frac{1}{nRT}\frac{\partial\gamma}{\partial \ln C}$$

where Γ is the surface excess, γ, surface tension, C, concentration of the detergent and $\boldsymbol{R}$ and T are gas constant and temperature, respectively. n is expected, from theoretical considerations, to be unity in the presence of large excess of salts

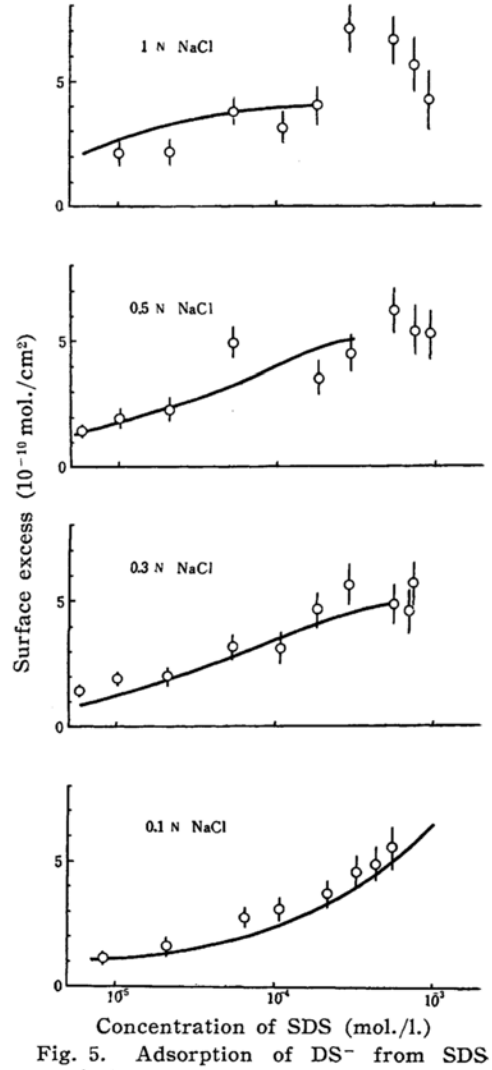

Fig. 5. Adsorption of DS⁻ from SDS solution containing sodium chloride. Full lines represent calculated relations from surface tension vs. logarithmic concentration curves by using the Gibbs adsorption equation of $n=1$.

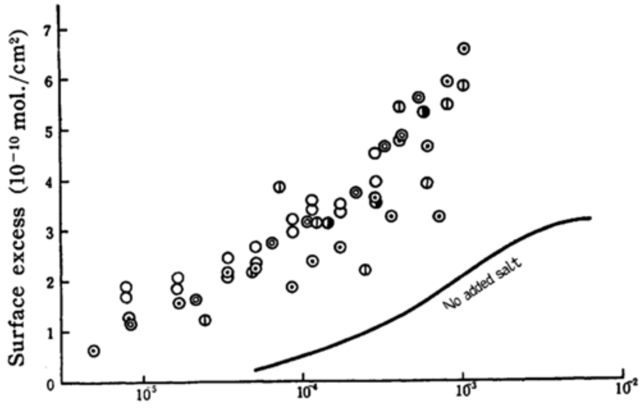

Fig. 6. Effect of added electrolytes on the adsorption of DS$^-$, 29±1°C. Concentration of electrolytes are all 0.1 N.
◎ NaCl, ◑ KCl, ⊙ $MgCl_2$, ⦶ $MnCl_2$, ○ $AlCl_3$.

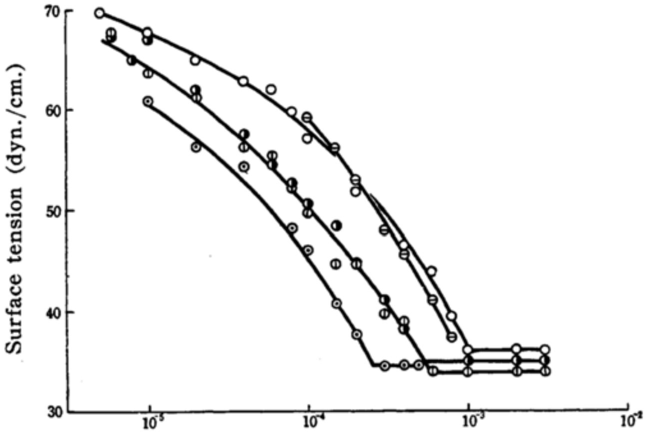

Fig. 7. Effect of added electrolytes on the surface tension of SDS solution, 29±1°C. Concentrations of electrolytes are all 0.1 N.
○ NaCl, ⊖ KCl, ◑ $MgCl_2$, ⦶ $MnCl_2$, ⊙ $AlCl_3$.

or alkalis[5]. From the data in Fig. 4 we can calculate Γ of DS$^-$ in the presence of sodium chloride and check the Gibbs equation*. The results are shown in Fig. 5 for various concentrations of sodium chloride. From these figures it is reasonable to conclude that the Gibbs adsorption equation of $n=1$ is a fair expression for the adsorption of DS$^-$ below cmc in the presence of sodium chloride.

Next the effect of various inorganic electrolytes having no common ion with the detergent was measured. Some salts made precipitates even in the dilute solution of the detergent and so the kinds of salts investigated were limited. The salts used in the present experiment were potassium chloride, magnesium chloride, manganous chloride and aluminum chloride and SDS was dissolved in the aqueous solution of each electrolyte of the concentration of 0.1 N. The relation between the surface excess of DS$^-$ and SDS concentration in the presence of 0.1 N inorganic electrolytes is shown in Fig. 6. From this figure we can see that the presence of excess of inorganic salts makes considerable increase in the adsorption of the detergent, regardless of the type of the salts added.

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* Strictly speaking, the concentration in the Gibbs equation should be replaced by the activity. However it may not cause serious errors to use concentration instead of activity *below cmc* of the detergent even in the presence of excess salt as in the present experiment[2,3].

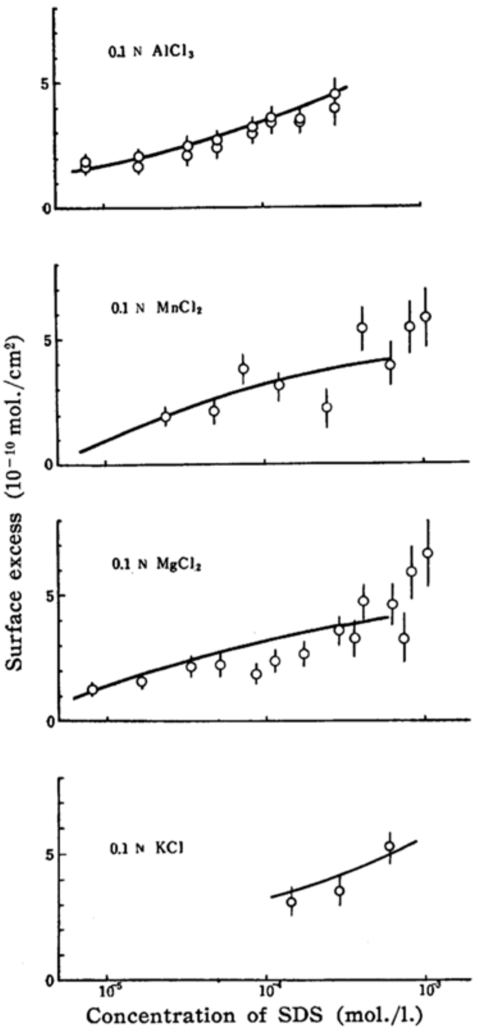

Fig. 8. Adsorption of DS^- from SDS solution containing 0.1 N excess of salt. Full lines represent calculated relations from surface tension vs. logarithmic concentration curves by using the Gibbs adsorption equation of $n=1$.

The surface tension vs. concentration relation of these systems is shown in Fig. 7. It is interesting to note that the surface tension decreases regularly with the valency of cation of added salts, while the surface excess shows no such regular relations.

Using the data in Fig. 7, the surface excess was calculated by the Gibbs equation putting $n=1$ and compared with the observed value. The results are plotted in Fig. 8. From these results it will be possible to say that the Gibbs equation of $n=1$ represents approximately the experimental values of surface adsorption of DS^- even in the presence of inorganic salts having no common ions with the detergent.

Summary

The direct measurement of the adsorption of ^{35}S labelled dodecyl sulfate ion at the solution surface and the measurement of the surface tension were carried out on the aqueous solutions of sodium dodecyl sulfate containing a given concentration of an excess salt. The salt concentrations studied were 0.01, 0.1, 0.3, 0.5 and 1 N for sodium chloride, and 0.1 N for potassium-magnesium, manganous and aluminum chlorides.

1. The adsorption of dodecyl sulfate ion reaches equilibrium within one minute for all the systems under investigation.
2. The presence of excess of salt gives rise to the remarkable increase in the adsorption of dodecyl sulfate ion, but at the concentrations of excessive salts of about 0.1 N or more, the effects of the concentration and nature of the salts on the adsorption of dodecyl sulfate ion are not so appreciable.
3. The adsorption of dodecyl sulfate ion was well expressed by the Gibbs adsorption equation of $n=1$ for the systems under investigation.

In conclusion the authors express their hearty thanks to Professor T. Sasaki of Tokyo Metropolitan University for his kind advice and encouragement in the course of this study. The cost of this study was defrayed from the Chemical Research Grant of the Ministry of Education, to which the authors' thanks are also due.

Department of Chemistry
Faculty of Science
Kyusyu University
Fukuoka