A Study of the Adsorption of Detergents at a Solution-Air Interface by the Radiotracer Method. V. The Effect of Inorganic Salts on the Surface Behavior of the Dodecyl Sulfate Ion

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It has been known that certain inorganic salts promote the detergent action of soaps. These substances are known as builders. In studying the detergent action it is of importance to see the nature of the effect of these builders on the adsorption of the detergent. In the preceding paper[1], the effect of the cationic valencies of excess salts and the concentration of sodium chloride on the adsorption of dodecyl sulfate ion (DS^-) at the solution-air interface was measured; it was found that the presence of excess salt increases the rate and the amount of the adsorption of DS^- and that the adsorption takes place in accordance with the Gibbs adsorption isotherm. However, the effect of the anion on the adsorption has not yet been studied systematically. Therefore, we have attempted the measurement of the adsorption of DS^- in the presence of excess sodium salt with an anion of a different valency. The discussions of the surface behavior of DS^- are given for the results obtained in the present study as well as for those in the preceding paper[1].

Experimental

Dodecyl alcohol was distilled through a rectifying column of 65 plates using a reflux ratio of 15, the fraction distilling at 139°C/10 mmHg being collected. The melting point of dodecyl alcohol was 25.0°C. ^{35}S-labeled sodium dodecyl sulfate (SDS) was synthesized as described earlier[2]. To remove the unsulfated alcohol, the crystals of SDS were washed with ether for 50 hr. by using a Soxhlet apparatus.

Of the inorganic salts used, those of a guaranteed grade were used without purification, while those of an extra pure grade were purified by recrystallization.

The procedures used for the experiments were the same as described in the preceding paper[1,2], and the experiments were carried out at temperature 30±1°C.

Results and Discussion

The adsorption of DS^- and the surface tension were measured in the presence of excess (0.1 N) sodium salt of an anion of varying valency. In Fig. 1, the surface tension data are plotted against the logarithmic concentration of SDS. As seen in this figure, the surface tension vs. logarithmic concentration

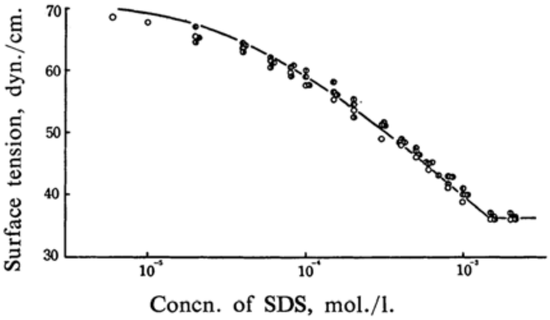

Fig. 1. Effect of excess (0.1 N) electrolyte on the surface tension of SDS solution, 30±1°C. Full line represents relationship calculated with Eq. 2.
○; NaCl ⦶; Na_2SO_4 ◐; $Na_3Fe(CN)_6$
◑; $Na_4Fe(CN)_6$

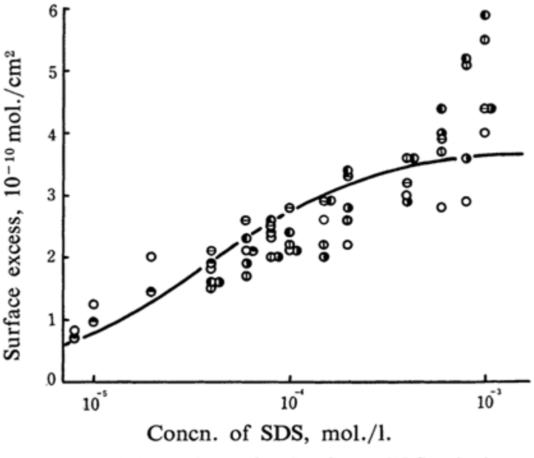

Fig. 2. Adsorption of DS^- from SDS solution containing excess (0.1 N) salt. Full line represents relationship calculated with Eq. 6.
○; NaCl ⦶; Na_2SO_4 ⊖; Na_2CO_3
◐; $Na_2Fe(CN)_6$ ◑; $Na_4Fe(CN)_6$
◓; $NaNO_3$

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

[2] R. Matuura, H. Kimizuka, S. Miyamoto and R. Shimozawa, ibid., 31, 532 (1958).

curves of the detergent solutions containing 0.1 N sodium salts are almost independent of the valencies of the anions of salts. This is true also for the relation between the amount of adsorption of DS$^-$ and the concentration of the detergent solution, as is shown in Fig. 2, although the measured values scatter randomly to some extent in this case.

In Fig. 3, the surface tension of SDS solutions containing excess salt of chlorine with a cation of varying valency, together with the case of sodium chloride of varying concentrations, is plotted against the logarithmic concentration of SDS. It is clear from this figure that the surface tension of the SDS solution decreases with an increase in the valency of the cation of the same normal concentration and decreases in the presence of the same salt (sodium chloride) with an increase in the concentration of the salt.

From the results of Figs. 1 and 3, it may be said that the surface tension lowering of the SDS solution due to the excess salt is governed not by the ionic strength, but by the normality when the sodium salts are used; it is also very much affected by the valency of cation when the various metal salts are used even with the same normality.

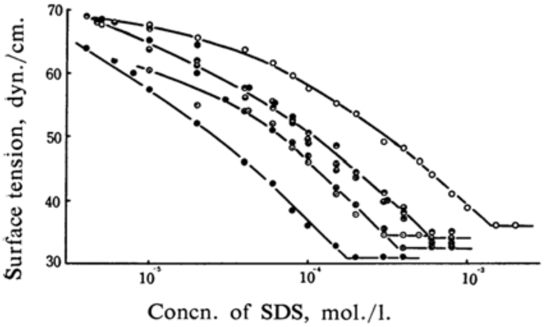

Fig. 3. Effect of excess electrolyte on the surface tension of SDS solution, 29.5± 1.5°C. ○; 0.1 N NaCl ⊕; 0.3 N NaCl ⊗; 0.5 N NaCl ●; 1 N NaCl ◓; 0.1 N $MgCl_2$ ◒; 0.1 N $MnCl_2$ ⊙; 0.1 N $AlCl_3$

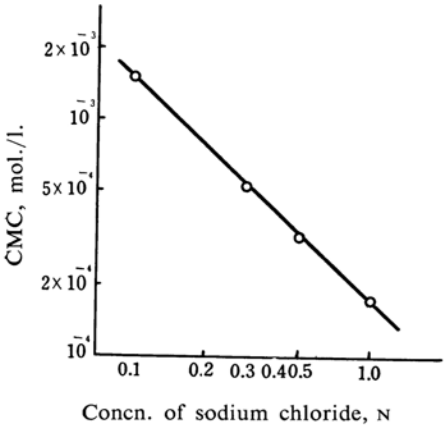

Fig. 4. Effect of concentration of sodium chloride on the CMC of SDS, 29±1°C.

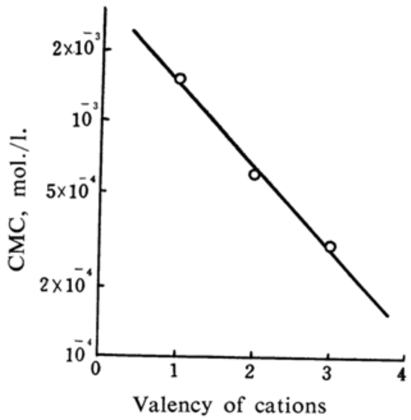

Fig. 5. Effect of added electrolyte on the CMC of SDS, 29±1°C. Concentrations of sodium chloride, magnesium chloride, manganous chloride and aluminum chloride are all 0.1 N.

The change in the value of critical micelle concentration (CMC), C_m, with the concentration of sodium chloride is shown in Fig. 4 and that with the valency of cation, in Fig. 5. As shown in Fig. 4, log C_m is linear against the logarithmic concentration of sodium chloride; this is a relation similar to that obtained by Corrin and Harkins[3]. In Fig. 5, log C_m is linear against the valency of the cation. This does not agree with the theory of Shinoda, who expected linearity between log C_m and the reciprocal of valency[4]. Though the effect of a high valent cation on the CMC of SDS solution was studied by Lange[5], he did not find this relation. It must, however, be noted here that the pH of the solution depends on the kind of electrolyte, so that the dependence of CMC upon the valency will require more detailed investigation. In Fig. 6, the surface pressure, π_m, at CMC is plotted against the concentration of salt as well as the valency of cation. This figure shows an increase in π_m with the concentration of sodium chloride, but at the normal concentration the valency of the anion has little effect on the value of π_m and the effect of the valency of the cation is not so appreciable.

Now we can put the reduced quantities as:

$$\phi=\pi/\pi_m, \quad X=C/C_m \tag{1}$$

where π denotes a surface pressure of the

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[3] M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 682 (1947).

[4] K. Shinoda, This Bulletin, **28**, 340 (1955).

[5] H. Lange, *Kolloid-Z.*, **121**, 66 (1951).

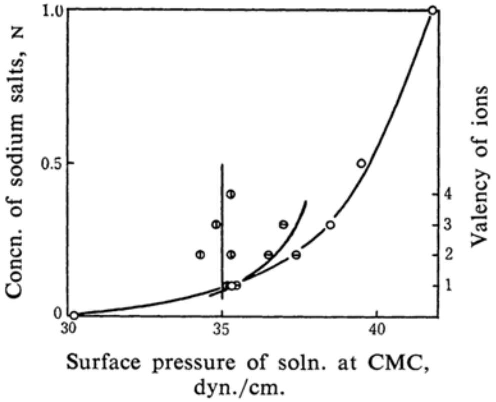

Fig. 6. Effects of salt concentration and of valency of cation on surface pressure of solution at CMC.
○ ; Effect of concentration of sodium chloride
⊖ ; Valency effect of cations
⦶ ; Valency effect of anions

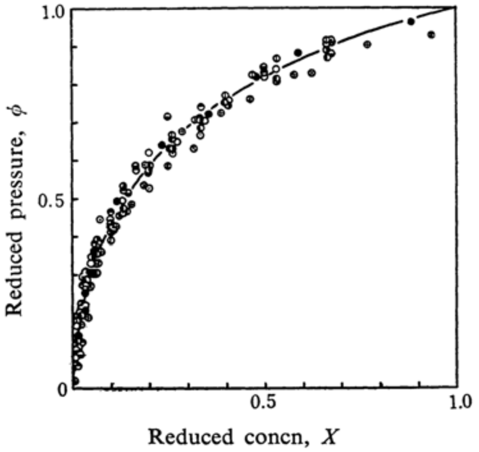

Fig. 7. Reduced pressure vs. reduced concentration.
○ ; 0.1 N NaCl ⊕ ; 0.3 N NaCl
⊗ ; 0.5 N NaCl ● ; 1 N NaCl
◓ ; 0.1 N $MgCl_2$ ◒ ; 0.1 N $MnCl_2$
⊙ ; 0.1 N $AlCl_3$ ⦶ ; 0.1 N Na_2SO_4
◐ ; 0.1 N $Na_3Fe(CN)_6$ ◑ ; 0.1 N $Na_4Fe(CN)_6$

solution of concentration, C. The ϕ vs. X curves are plotted as shown in Fig. 7. This figure indicates that the surface tension vs. concentration curves can be reduced approximately to the same one, regardless both of the concentration of the excess salt and of the type of salt when we use reduced quantities.

The full line in Fig. 7 shows the calculated relation by using the equation

$$\phi=(1/b)\cdot\ln\{1+(e^b-1)X\} \tag{2}$$

where b is a constant. The value of b is 3.7 in the present case. Belton and Evans[6] considered the ideal mixture in which the surface tensions of the solution, solvent and solute are γ, γ_A and γ_B respectively; they derived a relation between the surface tension and the mole fraction of solute x:

$$\exp(-\gamma\omega/\boldsymbol{k}\boldsymbol{T})=(1-x)\exp(-\gamma_A\omega/\boldsymbol{k}\boldsymbol{T}) \\ +x\exp(-\gamma_B\omega/\boldsymbol{k}\boldsymbol{T}) \tag{3}$$

where ω denotes the occupied area per molecule and $\boldsymbol{k}$ and T are Boltzmann constant and absolute temperature respectively. Equation 3 can be reduced to Eq. 2 by putting $x=X$ and

$$b=(\gamma_A-\gamma_B)\omega/\boldsymbol{k}\boldsymbol{T}$$
$$\phi=(\gamma_A-\gamma)/(\gamma_A-\gamma_B) \tag{4}$$

It may, therefore, be pointed out that the solution of SDS containing excess salt behaves approximately as if it were the ideal mixture consisting of the salt solution, regarded as a solvent, and the detergent solution at CMC containing a given concentration of salt, regarded as a solute. Thus it may be supposed that the reduced quantities are the suitable expressions in studying the detergent solution.

The Gibbs equation is expressed by:

$$\Gamma=(1/n\boldsymbol{R}\boldsymbol{T})\cdot(\partial\pi/\partial\ln C) \tag{5}$$

where Γ is the surface excess, $\boldsymbol{R}$, gas constant, and n is put unity in the case of excess salts. Differentiating Eq. 2 and combining it with Eq. 5, we obtain a reduced adsorption isotherm

$$\boldsymbol{R}\boldsymbol{T}\Gamma/\pi_m=(e^b-1)X/b\{1+(e^b-1)X\} \tag{6}$$

The full lines in Figs. 1 and 2 show calculated relations by using Eqs. 2 and 6 respectively. Agreements between observed and calculated values are satisfactory.

Summary

The adsorption of ^{35}S-labeled dodecyl sulfate ion in the presence of excess sodium salts with anions of various valencies was measured directly by the radiotracer method. The anions of the excess salts were chloride, nitrate, carbonate, ferricyanide and ferrocyanide ions, and the concentrations of the excess salts were all 0.1 N. It was found that the adsorption of dodecyl sulfate ion increased remarkably due to the presence of the excess salt and that the surface tension curves and the adsorption isotherms were almost independent of the type of anions.

The behavior of dodecyl sulfate ion was discussed by using the result of the present study together with the previous one, in which the effect of cationic valency and the salt concentration was studied. The logarithmic value of CMC was found to be linear against the logarithmic concentration of excess sodium

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[6] J. W. Belton and H. G. Evans, *Trans. Faraday Soc.*, **41**, 1 (1945).

chloride and against the valency of cation when the concentrations were all 0.1 N.

The reduced surface pressure and the reduced concentration referred to CMC were proposed, and it was found that the surface tension data of the solutions of sodium dodecyl sulfate containing various kinds of salts and varying concentration of sodium salts were correlated approximately to one curve regardless both of the types and the concentrations of the excess salts. The curve was well expressed by the reduced equation for the surface pressure as a function of the reduced concentration. By combining the reduced equation with the Gibbs equation of $n=1$, the reduced adsorption isotherm was derived.

It was shown that these reduced equations enable us to reproduce the surface tension and adsorption data of the solutions of sodium dodecyl sulfate in the presence of sodium salts with varying valencies of anions.

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