The Study of Adsorption of Detergents at a Solution-Air Interface by Radiotracer Method. II. The Kinetics of Adsorption of Sodium Alkyl Sulfates

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It is usual in the case of the solution of detergents that a considerable time is required to attain true equilibrium of adsorption at the solution-air interface. The process has been studied chiefly from the measurement of the change in surface tension with time. The suggestion that the diffusion of solute to the surface is a cause of the alteration of surface tension with time was first made by Milner[1], and equations to describe the phenomena in terms of diffusion have been deduced by Bond and Puls[2], Ross[3], Ward and Tordai[4], Bartholomé and Schäfer[5], Lange[6] and Fordham[7]. However, it has been proved that there are many cases in which the process can not be explained in terms of simple diffusion alone, and the factors governing the adsorption rate other than diffusion have been proposed. For example, the concept of energy barrier has been introduced by Doss[8], Blair[9] and Addison[10].

In the preceding paper[11] the Gibbs adsorption equation has been checked in the case of sodium dodecyl sulfate, tetradecyl sulfate and hexadecyl sulfate at the solution-air interface. It is perfectly clear that the Gibbs equation refers only to the adsorption equilibrium. It has nothing to do with the process of reaching the equilibrium, and so to calculate the surface excess at the stage of non-equilibrium from surface tension by using the Gibbs equation is incorrect. In order to study the kinetics of adsorption, therefore, it is preferable to measure the change in the adsorbed amount with time directly. By using radioisotopes this can easily be done. The method is simple and accurate, and is most suitable since the adsorption can be measured at a liquid surface without any mechanical disturbances. It is the purpose of the present experiment to measure the rate of adsorption of sodium alkyl sulfates at the solution-air interface by radiotracer method and to make discussions as to the theories of the adsorption rate presented by earlier authors.

Experimental

Surface active substances used in the present experiment were the same as those in the preceding paper[11], i. e., sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS). Labelling these compounds with S-35 was described earlier[11].

The counting apparatus was also the same as that used in the preceding paper[11]. After the formation of a fresh plane surface of a detergent

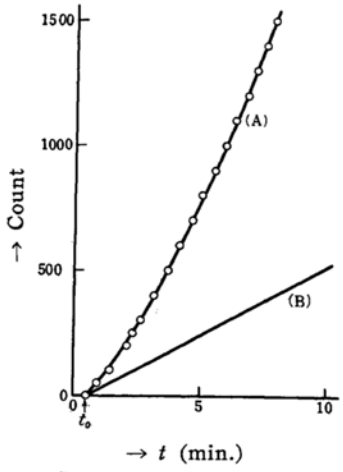

Fig. 1. Count vs. time curves for the solution of SHS (A) and sulfuric acid (B). Concentration, 4.24×10^{-6} mole/l.

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[1] S. R. Milner, *Phil. Mag.*, (6), **13**, 96 (1907).

[2] W. N. Bond and H. O. Puls, ibid., (7), **24**, 864 (1937).

[3] S. Ross, *J. Am. Chem. Soc.*, **67**, 990 (1945); *J. Phys. Chem.*, **49**, 377 (1945).

[4] A. F. H. Ward and L. Tordai, ibid., **14**, 453 (1946).

[5] E. Bartholomé and K. Schäfer, *Melliand Textilber.*, **31**, 487 (1950).

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[8] K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939); **87**, 272 (1939).

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solution, the measuring arrangement was quickly set in and the count from the solution was measured with time. An example is shown in Fig. 1 (curve A). The curve B in the same figure shows a change in the counting with time of a sulfuric acid solution with the same concentration and specific activity as the detergent solution. The two series of measurements should be done under exactly the same conditions. t_0 in Fig. 1 is the starting time of counting. The tangent of the curve at any time t is clearly the intensity of radiation from the bulk of the solution, I_i, plus that from the adsorbed layer at that time, $I_{s(t)}$. The intensity of radiation from sulfuric acid solution does not show any change with time and it can be regarded as equal to I_i since no surface adsorption will take place with sulfuric acid solution of so low a concentration as in the present experiment. Then,

$$I_{s(t)} = (I_i + I_{s(t)}) - I_i \tag{1}$$

i. e., the counting rate at time t of the surface layer can be obtained from the difference between the counting rate of the detergent solution at that time and that of sulfuric acid solution. The surface excess at time t, Γ_t, is calculated from $I_{s(t)}$ by using the following relation;

$$\Gamma_t = I_{s(t)}/SA \tag{2}$$

where S is the specific activity of the radioactive substance and A is the surface area of the solution. S can be determined as in the preceding paper[11].

Results

The change in adsorption with time of SDS, STS and SHS at the solution-air interface is plotted in Figs. 2, 3 and 4, respectively. The abscissa is represented as the square root of time for the convenience of discussions.

Discussions

It is seen from Figs. 2, 3 and 4 that at the initial stage of adsorption the surface excess of the detergents is proportional to the square root of time, i. e., the adsorption at constant temperature can be expressed by the relation,

$$\Gamma_t = Kt^{1/2} \tag{3}$$

were, t is the time of aging and K is a constant independent of time but dependent on the concentration of the detergent solution. When K is plotted against concentration, C, approximately linear relation can be found as shown in Fig. 5, i.e.,

$$K = K_0C \tag{4}$$

where K_0 is a constant characteristic of each detergent. From Eqs. 3 and 4 the

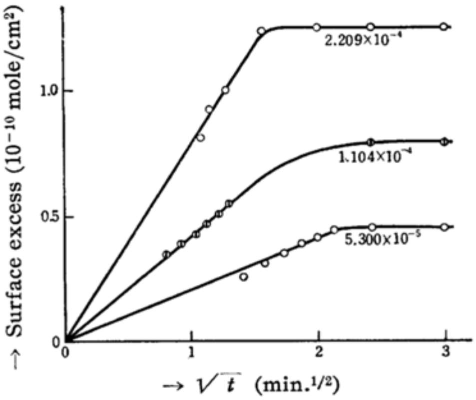


Fig. 2. Surface excess vs. time curves of SDS, at 28±1°C. Numericals of each curve represent the concentration of the detergent solution in mole/l.

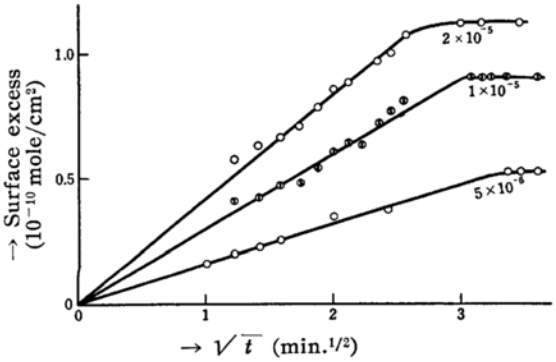


Fig. 3. Surface excess vs. time curves of STS, at 28±1°C. Numericals of each curve represent the concentration of the detergent solution in mole/l.

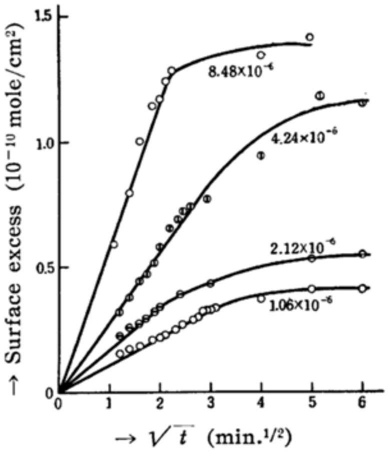
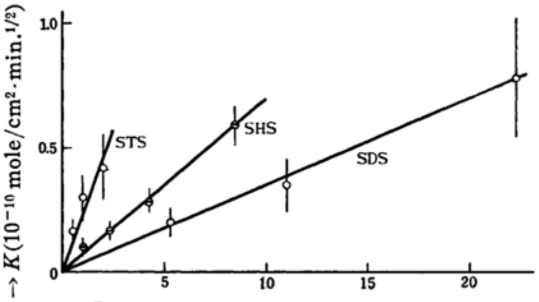


Fig. 4. Surface excess vs. time curves of SHS, at 28±1°C. Numericals of each curve represent the concentration of the detergent solution in mole/l.



→ Concentration (10^{-5} mole/l. for SDS and STS, 10^{-6} mole/l. for SHS)

Fig. 5. K vs. concentration of detergents at 28±1°C.

following relation is obtained;

$$\Gamma_t = K_0 C t^{1/2} \tag{5}$$

Now the simple diffusion theory[4] tells us that the surface excess at time t, Γ_t, is given by the relation,

$$\Gamma_t = 2C(Dt/\pi)^{1/2} \tag{6}$$

where D is the diffusion coefficient of the solute molecules. At first sight it is seen that Eq. 6 is similar in form to Eq. 5, and this similarity of the two equations may seem to lead to the conclusion that the rate of adsorption is determined solely by the diffusion of solute molecules from the bulk phase to the surface layer. But further insight makes it clear that discrepancy is involved in the simple diffusion theory. If the simple diffusion theory could be applied to the present case, K_0 in Eq. 5 should be equal to $2(D/\pi)^{1/2}$ in Eq. 6. Then we should be able to calculate the diffusion coefficient from the experimental values of K_0. The calculated values of diffusion coefficient of three alkyl sulfates used are shown in Table I as D_{calc}. In order to check the diffusion theory it is necessary to compare these values of D_{calc} with the observed values of diffusion coefficient. We could not find in any literature the experimental values of diffusion coefficient of sodium alkyl sulfates in aqueous solutions, but we can estimate the values from conductivity data of Lottermoser and Püschel[12] by using the Nernst's equation,

$$D = \Lambda_0 \boldsymbol{R} T / |Z| \boldsymbol{F}^2 \tag{7}$$

where Λ_0 is the conductivity at infinite dilution of surface active ion with the valency Z and $\boldsymbol{F}$, $\boldsymbol{R}$ and T are Faraday constant, gas constant and absolute temperature, respectively. The estimated values of diffusion coefficient for three alkyl sulfate ions used are shown in Table I as D_{est}. These values are, of course, diffusion coefficients at infinite dilution, but the concentrations so small as in the present experiment would not alter the values appreciably.

TABLE I

COMPARISON OF DIFFUSION COEFFICIENTS

Detergents	SDS	STS	SHS
Temp. (°C)	28±1	28±1	28±1
D_{calc}(cm^2/sec.)	1.60×10^{-9}	7.69×10^{-8}	6.32×10^{-7}
D_{est}(cm^2/sec.)	6.80×10^{-6}	4.54×10^{-6}	4.01×10^{-6}

As seen from Table I the calculated values of the diffusion coefficient are in general much smaller than the estimated ones. Moreover, the most embarrassing point is that the diffusion coefficient calculated by the simple diffusion theory decreases considerably with decrease in the chain length of the detergent molecule. This is quite unreasonable. Therefore, we can conclude that the simple diffusion theory can not explain the rate of adsorption of sodium alkyl sulfates at the solution-air interface under the conditions of the present experiment.

Salley et al.[13] measured the rate of adsorption of Aerosol OTN at the solution-air interface by radiotracer method and obtained the rate equation,

$$\Gamma_t = k t^n \tag{8}$$

where k and n are constants. They found that n is nearly 1/2. They calculated the diffusion coefficient of sulfosuccinate ion from the experimental values of k by making use of the simple diffusion equation. The calculated diffusion coefficient was $0.7\sim2.2\times10^{-4}$ cm^2/min., which was, according to them, comparable to the observed value, $3\sim4\times10^{-4}$ cm^2/min. However, we suppose that the agreement is not so good as to confirm the validity of the simple diffusion theory, and various surface active compounds, especially with varying chain length, should be examined in order to check the diffusion theory.

In the case of the adsorption of surface active electrolytes, such as those used in the present experiment, it is reasonable to take the energy barrier idea into consideration. Let λ be the energy barrier to the adsorption, then the rate equation[9] may be given by

$$\Gamma_t = 2C(Dt/\pi)^{1/2} \exp(-\lambda/\boldsymbol{R}T) \tag{9}$$

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[12] A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933).

[13] D. J. Salley, A. J. Weith, Jr., A. A. Argyle and J. K. Dixon, *Proc. Roy. Soc.*, **A203**, 42 (1950).

in which the simple diffusion equation is combined with the idea of energy barrier. Tentatively we applied Eq. 9 to the present case and calculated the energy barrier to the adsorption of three alkyl sulfates used in the present experiment. That is, from Eqs. 5 and 9

$$K_0 = 2(D/\pi)^{1/2} \exp(-\lambda/\boldsymbol{R}T) \qquad (10)$$

Using the value of D, estimated from the conductivity data of Lottermoser and Püschel, and K_0, obtained in the present experiment, the values of energy barrier were calculated*. They are shown in Table II.

TABLE II

ENERGY BARRIER, λ, TO THE ADSORPTION

Detergents	SDS	STS	SHS
Temp. (°C)	28±1	28±1	28±1
Energy barrier, λ, (kcal./mole)	2.5	1.2	0.6

We could not compare the calculated energy barrier with the observed one, and therefore the validity of the energy barrier theory has not been established. This point will be discussed by further study of the adsorption rate, especially in the presence of inorganic electrolytes.

Summary

The rate of adsorption of sodium dodecyl sulfate, sodium tetradecyl sulfate and sodium hexadecyl sulfate at the solution-air interface has been measured by radiotracer method. It has been found that the surface excess of a detergent is proportional to the concentration of the solution and the square root of time of aging at the initial stage of adsorption. The simple diffusion theory has been checked and it has been found that the results of the present experiment can not be explained by the simple diffusion theory. The idea of energy barrier has tentatively been applied and the values of energy barrier have been calculated.

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* Strictly speaking, we should calculate λ from the slope of $\ln K_0/2(D/\pi)^{1/2}$ vs. $1/T$ plot.