# *The Study of Adsorption of Detergents at a Solution-Air Interface by Radiotracer Method. IV. The Valency and Concentration Effects of Added Electrolytes on the Adsorption of Alkyl Sulfate Ion*

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The preceding study on the effect of excess electrolytes on the adsorption of dodecyl sulfate ion using the radiotracer method has confirmed directly the fact that the presence of excess electrolytes increases both the equilibrium amount and the rate of adsorption of the dodecyl sulfate ion[1], the result which was deduced by a number of authors from surface tension measurements of the solution[2]. However, in the presence of a large excess of electrolytes the rate of adsorption was too rapid to be measured accurately and also the adsorption isotherm was nearly independent of the type of added electrolytes.

We may expect to obtain further data concerning the effects of added electrolytes on the rate and the amount of adsorption of the detergent if we explore the region of the more dilute concentrations of the added electrolytes and/or the detergent. The present paper describes the results of such experiments and the discussions about them.

## Experimental and Results

The method of preparation and purification of the samples and the procedure used for the experiments have already been described[1,3]. The specific activities of the radioactive sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS) and sodium hexadecyl sulfate (SHS) used were ca. 10 mc. per millimole. The temperatures of the experiments were 29.5 ±1.5°C.

In the study on the valency effect, the concentrations of electrolytes were all $10^{-4}$ mol./l., and those of SDS ranged from $5\times10^{-6}$ to $5\times10^{-5}$ mol./l. In the study on the effect of the excess salt the concentrations of detergents were $4\times10^{-6}$ mol./l. for SDS and $2\times10^{-6}$ mol./l. for STS and SHS and those of salt were changed from $10^{-3}$ mol./l. to 1 mol./l.

The rate of adsorption and the adsorption isotherm of dodecyl sulfate ion ($DS^-$) in the presence of electrolytes are shown in Figs. 1 and 2, respectively. In Fig. 1, $K$ represents the constant in the rate equation

$$\Gamma_t = K\sqrt{t} \quad (1)$$

where $\Gamma_t$ denotes the amount of adsorption at time $t$[4].

As is seen from these figures, both the rate and the equilibrium amount of the adsorption of $DS^-$ increase with the increase in cationic valency of the electrolyte, while they are almost independent of the anionic valency. Table I shows the values of rate constant $K_0$ of the equation

$$K = K_0 C \quad (2)$$

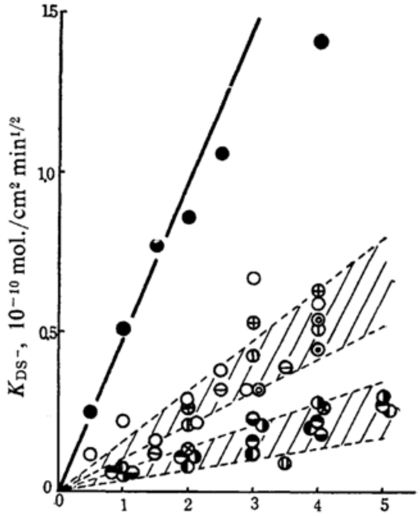

Fig. 1. Effect of added electrolytes on the rate of adsorption of $DS^-$, 29.5±1°C. Concentrations of electrolytes are all $10^{-4}$ mol./l.

I { ◑ NaCl, ◐ $Na_2SO_4$, ⦷ $Na_2CO_3$, ◓ $K_3Fe(CN)_6$, ◒ KCl.

II { ○ $MgCl_2$, ⦶ $CoCl_2$, ⊖ $HgCl_2$, ⊕ $MnCl_2$, ⊗ $Zn(CH_3COO)_2$, ◎ $CaCl_2$, ⊙ $Ca(OH)_2$.

III ● $AlCl_3$.

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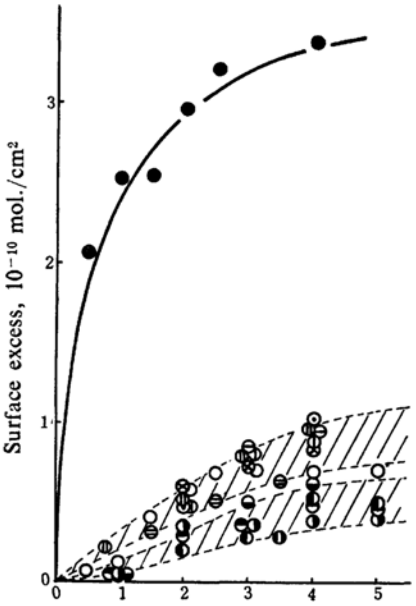
[1] R. Matuura, H. Kimizuka and K. Yatsunami, This Bulletin, 32, 646 (1959).

[2] N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, 34, 758 (1938); G. C. Nutting, F. A. Long and W. D. Harkins, *J. Am. Chem. Soc.*, 62, 1496 (1940), etc.

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

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



Concn. of SDS, $10^{-5}$ mol./l.

Fig. 2. Effect of added electrolytes on the equilibrium adsorption of $DS^-$, 29.5±1°C. Concentrations of electrolytes are all $10^{-4}$ mol./l.

I {◑ NaCl, ◐ $Na_2SO_4$, ◑ $Na_2CO_3$, ◒ $K_3Fe(CN)_6$ ◓ KCl.

II {○ $MgCl_2$' ⦶ $CoCl_2$, ⊜ $HgCl_2$, ⦶ $MnCl_2$, ⊙ $Zn(CH_3COO)_2$, ⊖ $CaCl_2$, ⊗ $Ca(OH)_2$.

III ● $AlCl_3$.

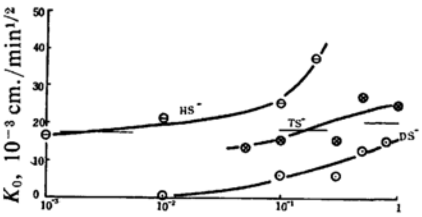
TABLE I. RATE CONSTANT $K_0$ OF THE ADSORPTION OF $DS^-$ IN THE PRESENCE OR ABSENCE OF ELECTROLYTE. THE CONCENTRATIONS OF SDS, $5\times10^{-6}\sim5\times10^{-5}$ mol./l.; THE CONCENTRATION OF ELECTROLYTE, $10^{-4}$ mol./l. $K_0$ IN $10^{-3}$ cm./min$^{1/2}$. 29.5 ±1.5°C

| | No added salt | Added electrolyte | | |
|---|---|---|---|---|
| | | Valency of cation | | |
| | | 1 | 2 | 3 |
| $K_0$ | 0.35±0.1 | 0.52±0.2 | 1.35±0.3 | 4.30±0.5 |

where $C$ is the concentration of SDS⁴⁾.

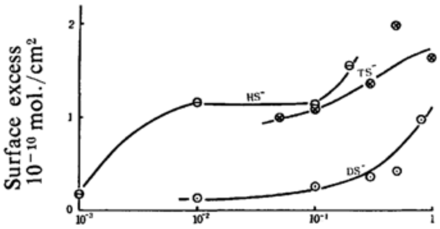
The value of $K_0$ in the absence of added electrolyte calculated according to the simple diffusion theory⁵⁾ is $22.8\times10^{-3}$ cm./min$^{1/2}$. It is seen from Table I that the rate constants increase in the presence of electrolyte, showing a greater increase the higher the cationic valency, but the values are less than the rate constant of the simple diffusion theory.

The effects of electrolyte concentrations on the rate constants and the equilibrium adsorptions of $DS^-$, tetradecyl sulfate ion ($TS^-$) and hexadecyl sulfate ion ($HS^-$) are shown in Figs. 3 and 4, respectively. These figures indicate that the presence of excess sodium chloride remarkably increases the equilibrium adsorption as well as the rate constants of the alkyl sulfate ions. It must be noted here that the rate constant does exceed the value of the simple diffusion theory when the concentration of the salt becomes great as indicated in the cases of $TS^-$ and $HS^-$. Unfortunately the diffusion coefficients of $TS^-$ and $HS^-$ in the presence of excess salt have not been known, and so we calculated the rate of adsorption by the simple diffusion theory using the diffusion coefficient in the absence of added electrolyte. But the condition described above will be held even when the diffusion coefficient in the presence of added salt is used, because it may generally be considered as less than that in the absence of salt*.



Concn. of NaCl, mol./l.

Fig. 3. Effect of salt concentration on the rate constant of adsorption of the alkyl sulfate ion. 29.5±1.5°C. Concentrations of detergents are $4\times10^{-6}$ mol./l. for SDS and $2\times10^{-6}$ mol./l. for STS and SHS. Horizontal lines indicate the values expected from the simple diffusion theory.



Concn. of NaCl, mol./l.

Fig. 4. Effect of salt concentration on the adsorption of the alkyl sulfate ion. 29.5± 1.5°C. Concentrations of detergents are $4\times10^{-6}$ mol./l. for SDS and $2\times10^{-6}$ mol./l. for STS and SHS.

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5) A. F. H. Ward and L. Tordai, *J. Chem. Phys.*, **14**, 453 (1946).

* We have measured the self-diffusion coefficient of $DS^-$ at the concentration of $4\times10^{-4}$ mol./l. in the presence (0.1 N) and absence of sodium chloride and found the values, at 25°C, to be $5.6\times10^{-6}$ and $6.5\times10^{-6}$ cm²/sec., respectively. We are going to measure the corresponding values of $TS^-$ and $HS^-$, the result of which will be published in a separate paper after the work has been completed.

## Discussion

The simple diffusion theory proposed by Ward and Tordai⁵⁾ assumed that the adsorption takes place as a result of the formation of the subsurface of zero concentration, which is taken to be the region of the thickness of a few molecular diameters being situated in the immediate vicinity of the surface. The formation of a subsurface of zero concentration is explained by the fact that the surface active solute finds a position of lower potential energy in the surface than in the bulk. According to this theory, at the initial stage of the formation of the adsorbed layer, the solute molecules will diffuse from the bulk to the subsurface more slowly than they do from the subsurface to the surface, on the assumption that the equilibrium is established instantaneously between the latter two regions.

It has, however, been shown that the simple diffusion theory fails to explain quantitatively our experimental results of the adsorption of alkyl sulfate ions without added inorganic electrolytes⁴⁾, and the present result also shows that the simple diffusion theory does not hold for the adsorption of $DS^-$ in the presence of a small concentration of inorganic electrolytes, as is shown in Table I. Also the results of the experiments on the adsorption of non-electrolytes from the solution so far reported by several authors can not be explained by the simple diffusion theory⁶⁾. All these results showed that the rate of adsorption is smaller than the value expected from the simple diffusion theory.

As the factors responsible for the delay in the rate of adsorption Blair⁶⁾ proposed an energy barrier for the adsorption of non-electrolytes and Doss⁷⁾ an electrical potential barrier for the surface active electrolytes. Some other factors, e. g., the reorientation⁸⁾ and the surface pellicle formation⁹⁾, have also been considered. Of course, these various factors taken together are responsible for the retardation of the adsorption rate of alkyl sulfate ions at the solution-air interface. It is difficult to cover the whole experimental result by any single theory. For example, let us consider Doss' theory of electrical potential barrier. According to this theory, the electrical double layer at the surface resists the adsorption of surface active ion owing to the electrical repulsion. The rate differs from the value of the diffusion theory, which may be regarded as being essentially identical with the simple diffusion theory, by a factor

$$\exp\left(-\frac{x\varepsilon\psi_0}{kT}\right) \tag{3}$$

where $x$ denotes the fraction of surface covered by the adsorbed molecules, $\varepsilon$, the elementary charge, $\boldsymbol{k}$, the Boltzmann constant and $T$, the absolute temperature. $\psi_0$ is given by

$$\psi_0 = -\frac{4\pi\rho}{D}\sqrt{\frac{1000\,DkT}{4\pi N\varepsilon^2\sum_i c_i z_i^2}} \tag{4}$$

where $\rho$ is the surface charge density at monolayer adsorption, $D$, the dielectric constant of medium, $N$, the Avogadro number and $c_i$, the concentration of $i$-th ion having valency $z_i$. Eqs. 3 and 4 predict that the rate of adsorption at the given amount of adsorption depends upon the ionic strength of the solution. From Fig. 1 and Table I it may be seen that the rate of adsorption does not depend on the anionic valencies in spite of their different ionic strengths of added electrolytes, but depends essentially on the cationic valencies. These facts can not be explained by Doss' theory mentioned above. Cassie and Palmer¹⁰⁾ deduced from their consideration on the structure of the adsorbed film, assuming Gouy-Chapman's diffuse double layer, that the film of long chain anions will be remarkably influenced by the presence of a high valent cation, while it will be independent of the nature of the anion in solution. Our result agrees with this view and also with observation on the surface²⁾ or interfacial tension¹¹⁾. Of course, the electrical double layer formed at the surface will be supposed to resist the adsorption of surface active ion, but the quantitative explanation for it should be given in a somewhat different way.

As the concentration of the added electrolyte becomes larger, the rate of adsorption of alkyl sulfates becomes faster until it reaches the value predicted by the simple diffusion theory in the case of $DS^-$, while in the cases of $TS^-$ and $HS^-$ the rate constants exceed the simple diffusion values, as shown in Fig. 3. It is not easy to explain by the prevailing theories the reason why the rates of adsorption of $TS^-$ and $HS^-$ exceed the values of simple diffusion theory in the presence of a large excess of electrolyte.

Addison¹²⁾ proposed that the difference between the dynamic and the static surface tension is a measure of the driving force for the adsorption, which is introduced in his theory

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6) C. M. Blair, Jr., ibid., **16**, 113 (1948).

7) K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939).

8) A. E. Alexander, *Trans. Faraday Soc.*, **37**, 15 (1941).

9) J. W. McBain and L. H. Perry, *Ind. Eng. Chem.*, **31**, 35 (1939); M. E. L. McBain and L. H. Perry, *J. Am. Chem. Soc.*, **62**, 989 (1940).

10) A. B. D. Cassie and R. C. Palmer, *Trans. Faraday Soc.*, **37**, 156 (1941).

11) C. Robinson, *Nature*, **139**, 626 (1937).

12) C. C. Addison, *J. Chem. Soc.*, **1944**, 477.

explicitly as the surface activity. At equilibrium there is a concentration gradient near the surface. Since the ordinary diffusion takes place from higher to lower concentrations, the equilibrium state may be supposed to be the state at which the osmotic force due to the concentration gradient is equilibrated with an adsorptive force such as the driving force suggested by Addison.

In general, both the driving force and the activation energy may be considered to be the factors responsible for the rate of adsorption. It may be pointed out here that the difference between the amount of solute in a dynamic surface and that in an equilibrium surface is a measure of the driving force and so the equilibrium adsorption becomes a measure of the driving force at the instant of the formation of the fresh surface. Thus the higher surface active molecule may drift to the surface faster than the lower surface active one providing the activation energy remains in the constant. The change in the rate of adsorption caused by the foreign substance should, therefore, be attributed not only to the change in activation energy, but also to the change in surface activity.

By comparing Figs. 1 and 2 it is seen that the presence of polyvalent cation increases both the rate and the amount of equilibrium adsorption of $DS^-$ at a given concentration of SDS. This means that the higher rate of adsorption should be related to the larger amount of adsorption in addition to the lowering of activation energy. This is also true for the case of Figs. 3 and 4. The fact that the rate constants of $TS^-$ and $HS^-$ exceed the predicted value of the diffusion theory indicates clearly that the surface activity should be taken into account in the theory of the rate of adsorption of detergent at the solution surface.

## Summary

The adsorption of dodecyl sulfate ion in the presence of various inorganic electrolytes whose concentrations are all $10^{-4}$ mol./l. and the adsorption of alkyl sulfate ions in the presence of the excess salt were measured by using S-35 labeled alkyl sulfates.

In the presence of various electrolytes, both the rate of adsorption and the equilibrium adsorption of dodecyl sulfate ion increase with the cationic valency of added electrolyte, while they are almost independent of the anionic valency.

In the presence of the excess salt, both the rate and the equilibrium adsorption of the alkyl sulfate ions increase with the salt concentration. With increasing concentration of salt the rate of adsorption of the dodecyl sulfate ion approaches the rate of the simple diffusion theory, while that of tetradecyl- and hexadecyl sulfate ion exceeds the value predicted by the simple diffusion theory.

It was pointed out that the higher rate of adsorption is attributed to the higher surface activity of solute.

The idea of surface activity was explicitly introduced in the explanation for the adsorption process and the discussions for the theories proposed earlier were given.

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