The Self-diffusion of Surface Active Agents in Nylon

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Adsorption of surface active agents on various solid surfaces such as metal, carbon, wool, cotton, acetate and polyamide fibers has been studied by many workers[1-5] as the fundamental contributions to the study of the physicochemical properties of detergents or as the first step to study the mechanism of detergency. However, the process of adsorption of detergents by the solid is rather complicated and there are a number of problems to be solved by further investigation.

We have studied[6] the adsorption of the surface active agents such as sodium dodecyl sulfate, sodium tetradecyl sulfate as well as inorganic ions such as sulfate, chloride, phosphate and calcium ions on the surface of nylon plate. The quantities of these substances taken up by nylon are very great and a very long time is required to reach an adsorption equilibrium. From these facts, it seems that the penetration of the adsorbed substances into the solid body plays an important role in the process of sorption and so the measurement of diffusion in solid is considered to be significant in a study of the adsorption of these substances to polymer solid.

In this paper, the self-diffusion rates in nylon

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of sodium dodecyl sulfate and sodium tetradecyl sulfate, and also of sulfuric acid and hydrochloric acid were studied, using the nylon plates and the radioactive tracers.

Experimental Method

The measurement was carried out by the surface radioactivity decrease method, which consists in measuring the decrease in radioactivity of the surface with the time due to the diffusion of the radioactive tracer into nylon. This method has the following advantages: the measurement is accomplished in a short diffusion time when the suitable β-ray energy such as that of ^{35}S is used and it is not necessary to use any particular arrangements.

A nylon plate was 2.5 mm. in thickness, 2.5 cm. ×2.5 cm. in size. It was cleaned by washing with ether, acetone and hot water before use.

The surface active agents used in this experiment were sodium dodecyl surfate (SDS) and sodium tetradecyl sulfate (STS). They were prepared from pure dodecyl alcohol and tetradecyl alcohol, respectively, and their purity was confirmed surface-chemically. The radioactive SDS and STS, both tagged with ^{35}S, were prepared from corresponding alcohols and radioactive sulfuric acid ($H_2{}^{35}SO_4$). Radioactive sulfuric acid ($H_2{}^{35}SO_4$) and hydrochloric acid ($H^{36}Cl$) were used for the measurement of diffusion of the sulfate ion and the chloride ion, respectively. The absorption coefficients of the β-rays of ^{35}S and ^{36}Cl in nylon were estimated using the sufficiently swollen nylon film (25μ in thickness), and the values, $321\,cm^{-1}$ for ^{35}S and $12.7\,cm^{-1}$ for ^{36}Cl were obtained.

Diffusion experiments were accomplished as follows: the nylon plates are immersed in various concentrations of each non-radioactive solution at 33°C for about two weeks in order that the nylon might sorb the solute by a complete equilibrium amount corresponding to each concentration. (It has been shown that the sorption equilibrium is accomplished completely under these circumstances.) They are taken up from the solution, blotted by filter paper, then immersed instantly in each radioactive solution of the same concentrations as the non-radioactive solution used, for the purpose of making a surface radioactive layer, probably, by surface exchange. They are stirred sufficiently for about 0.5~2 min., then the nylon plates are taken up, washed with a large amount of water for a few seconds, blotted with filter paper and counted instantly under the G-M tube. They are then fitted in a closed glass vessel of saturated humidity which is then kept in a thermostat. When the diffusion has progressed appropriately (about 20 hr. for SDS and STS, 4 hr. for H_2SO_4, 48 hr. for HCl at 33°C, respectively), the nylon plates are removed from the vessel and their radioactivity is counted in the same manner as before, and the ratio A/A_0 (A_0: initial counts of the surface of nylon, A: its counts at time t) is estimated. A/A_0 is given by the following equation[7,8]

$$A/A_0=[1-\mathrm{erf}\{(\mu^2Dt)^{1/2}\}]\exp(\mu^2Dt) \qquad (1)$$

where D is the self-diffusion coefficient of the diffusing ion, and μ is the absorption coefficient of the β-ray in nylon. A/A_0 can be plotted as a function of μ^2Dt and by using this graph D can be obtained from the measured value of A/A_0 since μ and t are known.

The quantity of each solute sorbed by nylon was measured by the same method as in the previous paper[6] and expressed as millimoles per kilogram of nylon, which was calculated by calibrating the decrease of counts owing to the absorption of radiation by nylon.

Radioactivity measurements carried out by means of a thin mica window G-M tube ($1.4\,mg./cm^2$) and the conventional scaler. For the purpose of establishing the counting area and avoiding the edge effect on counting, a brass ring 1 mm. think and 22 mm. in inner diameter was placed on the plate when it was counted.

The change of the efficiency of the counting equipment was always checked by a radioactive standard prepared on a nylon plate. Counting times were made so long that the standard counting error was less than 1%.

Results

To confirm the compatibility of the above diffusion equation (1) in these measurements the values of A/A_0 at various diffusing time were measured at 33°C with SDS and H_2SO_4 (Figs. 1 and 2). In these figures, the curves of solid line show the calculated values obtained by the above equation and the value of D at $A/A_0=0.5$. The points are the measured ones. It is seen that this equation can be applied to calculate the diffusion coefficient in these systems.

The sorption isotherms of each substance by nylon plate were measured by the radiotracers to estimate the quantities sorbed in nylon.

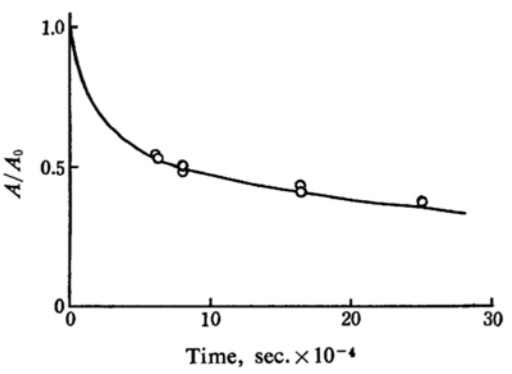

Fig. 1. The check of compatibility of the Eq. 1 by the diffusion of SDS at the concentration of 34 millimol./kg. in nylon at 33°C. The solid line is the calculated values and the points are the measured ones.

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[7] V. Linnenbom, M. Tetenbaum and C. Cheek, *J. Appl. Phys.*, 26, 932 (1955).

[8] F. Bueche, W. M. Cashin and P. Debye, *J. Chem. Phys.*, 20, 1956 (1952).

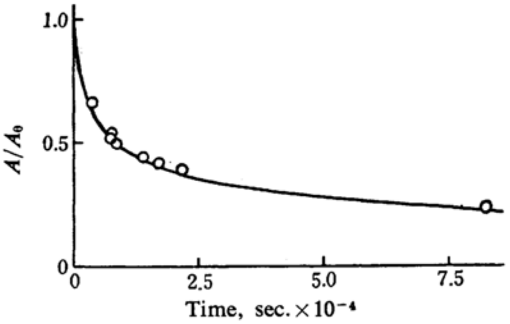

Fig. 2. The check of compatibility of the Eq. 1 by the diffusion of H_2SO_4 at the concentration of 63 millimol./kg. in nylon at 33°C. The solid line is the calculated values and the points are the measured ones.

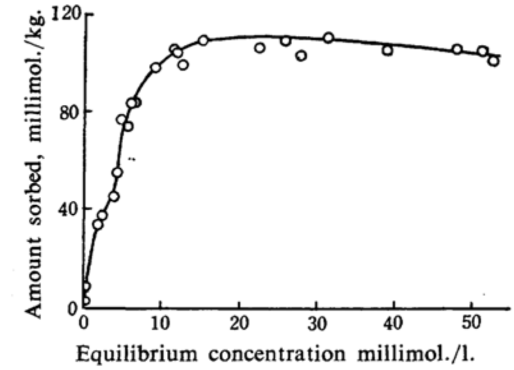

Fig. 3. The isotherm of the sorption of SDS by nylon plate at 33°C.

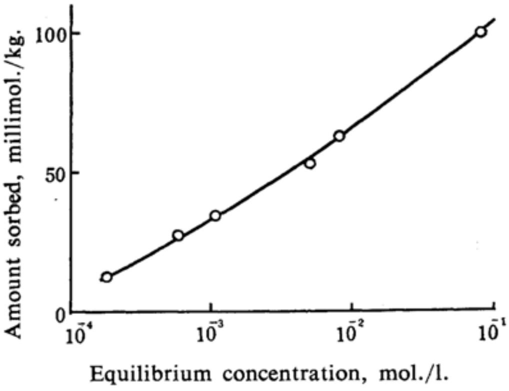

Fig. 4. The isotherm of the sorption of H_2SO_4 by nylon plate at 33°C.

The results for SDS and H_2SO_4 as examples are shown in Figs. 3 and 4, respectively.

The diffusion coefficients of SDS, STS, H_2SO_4 and HCl were measured at various concentrations of every solute in nylon. The results are shown in Figs. 5 and 6 and in Table I.

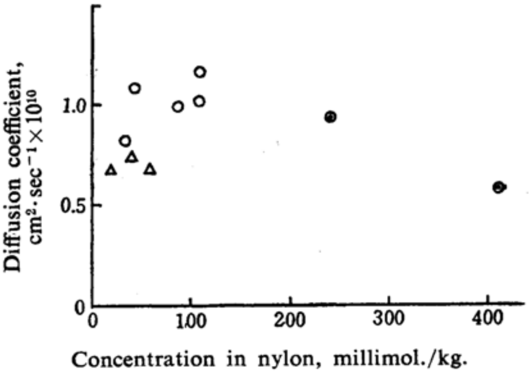

Fig. 5. Diffusion coefficient of SDS and STS at 33°C.

○ SDS
△ STS
⊙ The values of SDS obtained by the nylon plate which contained the large quantity of SDS by the lowering of the medium pH with HCl and KCl.

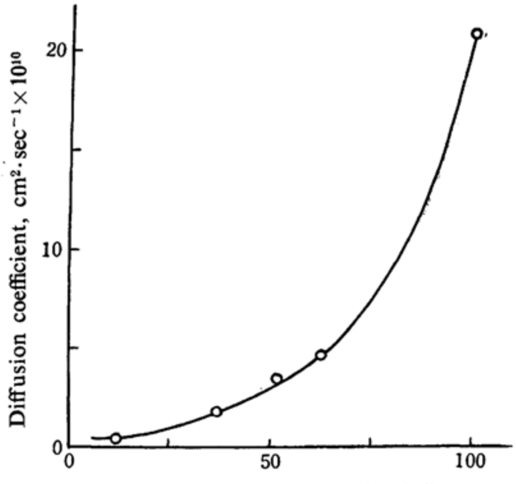

Fig. 6. Diffusion coefficient of H_2SO_4 at 33°C.

TABLE I. SELF-DIFFUSION COEFFICIENTS OF HCl AT 33°C

Concentration of HCl* mol./l.	Diffusion coefficient cm²·sec⁻¹×10⁹
10^{-1}	6.46
10^{-2}	0.120
10^{-3}	0.176

* The concentration of the solution described here is that which is in sorption equilibrium.

The diffusion coefficients of SDS and H_2SO_4 at various temperatures were measured to observe the effect of temperature on the diffussion and are shown in Table II. When log D is plotted against $1/T$, the straight lines are obtained as shown in Fig. 7, from which the

TABLE II. TEMPERATURE DEPENDENCE OF DIFFUSION COEFFICIENTS

Diffusing substance	Concentration in nylon (millimol./kg)	Diffusion coefficient $cm^2 \cdot sec^{-1} \times 10^{10}$					Activation energy, E cal./mol.
		−4°C	5°C	10°C	19°C	33°C	
SDS	102	0.00012	0.0053	0.0177	0.182	1.10	33400
H_2SO_4	63	0.0209	0.102	0.241	0.927	4.69	23200

activation energy E in the equation $D=D_0 \exp(-E/RT)$ was estimated and shown in the last column of Table II.

If the nylon sample is dried before or after the dipping in radioactive solution, the diffusion is little observed by this method at the room temperature.

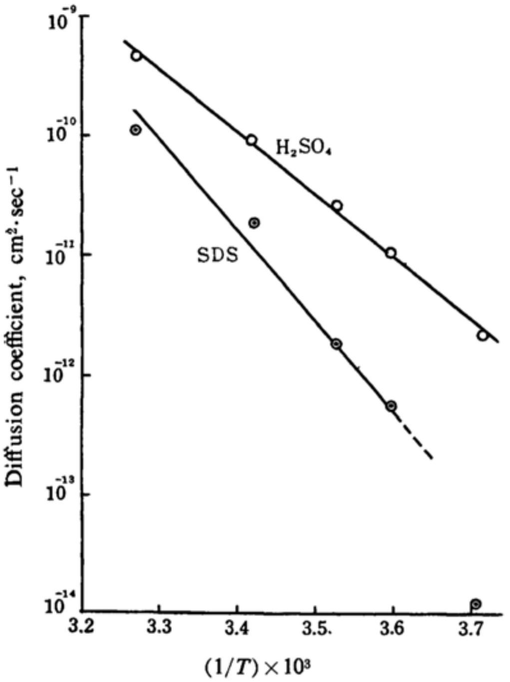

Fig. 7. Temperature dependence of diffusion coefficients of SDS (102 millimol./kg.) and H_2SO_4 (63 millimol./kg.).

Discussion

In this experiment the measurements of the self-diffusion rate were always carried out using sufficiently swollen nylon plates and it has been confirmed by weight that the swelling of each sample under the condition of the present experiment is constant throughout the whole diffusion process. The self-diffusion of the surface active agents or inorganic acids became remarkably slower as a nylon plate was dried and could not be observed at the room temperature in the completely dried state of nylon. It is evident, therefore, that these substances diffuse with the aid of water in nylon.

It is clear from the results of the present experiment that in the sorption of surface active agents and also of inorganic acids from their aqueous solutions by nylon, not only the surface phenomenon but also the diffusion into the solid body is responsible for its process towards equilibrium.

The self-diffusion coefficients of SDS and STS in nylon at 33°C are dependent, though not remarkably, on the concentration of each detergent in nylon as shown in Fig. 5. The values are comparable with those of several dyes reported by some workers[9,10], but they are much smaller than the values[11] in aqueous solutions. We suppose that the internal body of nylon is a gel of extremely close-packed network structures, water being included and forming fine canals among them. The molecules of detergent will penetrate along these canals into the internal structures of nylon, but they are immobilized by the adsorption sites to a large extent and so the rate of diffusion is reduced considerably compared with the free diffusion in aqueous systems. It is considered that the jumping of the adsorbed molecules from site to site occurs just as in the diffusion of ions in their crystals. Indeed the activation energies for diffusion of SDS and sulfuric acid are 33.4 and 23.2 kcal. per mole respectively as shown in Table II. These values are much greater than the values of many substances in aqueous systems, rather resembling these in solid crystals[12].

We suppose that the interaction of ionic detergents and nylon takes place not only by ionic force but also by van der Waals force, since the amount of detergents sorbed by nylon is much larger than that of simple inorganic ions which are considered to be bound to nylon mainly by ionic interaction[6]. This is confirmed by the fact that the amount of detergents taken up is also much larger than the value corresponding to the amine content of nylon[13,14]. The sorption of sulfuric acid

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[14] F. C. McGrew and A. K. Schneider, *J. Am. Chem. Soc.*, **72**, 2547 (1950).

and hydrochloric acid will be caused mainly by the attachment of these substances to the amino groups or to the amide groups in the molecule of nylon. From this point of view, therefore, it is supposed that there is also a difference between detergent and inorganic acid in the mechanism of diffusion. Indeed as shown in Figs. 5 and 6, the diffusion coefficient of the detergent does not change markedly with concentration of the detergent in nylon, while that of the inorganic acid increases remarkably with its concentration. At present, however, it is difficult to give a precise mechanism for the diffusion of the detergent and inorganic acid in nylon. This will be discussed after further investigation has been performed.

Summary

The self-diffusion rates of sodium dodecyl sulfate, sodium tetradecyl sulfate, sulfuric acid and hydrochloric acid in nylon containing various amounts of each solute and their temperature dependence were measured by the surface radioactivity decrease method using ^{35}S and ^{36}Cl.

From the experimental results, it has become clear that the diffusion of the solute in nylon is important in the process towards the attainment of sorption equilibrium of these substances by nylon, and in this case the presence of water in nylon is necessary for the diffusion to take place appreciably. The diffusion coefficients were much smaller than those in their aqueous solutions.

The diffusion rates of the surface active agents depended little on the concentration in nylon compared with those of the inorganic acids. The diffusion rates of sulfuric acid and hydrochloric acid depended largely on their concentration in nylon. This will be due to a difference of the mechanism of diffusion between the former and the latter.

The activation energies of SDS and sulfuric acid for diffusion were considerably great and approximated to those of many substances in solid.

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