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Desorption of Spread Monolayer of 1-Dodecanol into Aqueous Sodium Dodecyl Sulfate Substrate

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The process of desorption of dodecanol monolayer into the aqueous sodium dodecyl sulfate (SDS) solutions of varying concentrations was studied by the surface tension measurement. The rate of desorption in its early stage obeyed the simple diffusion law and the plot of logarithms of surface pressure against the square root of time showed a linear relationship. The rate constant of desorption decreased slightly and linearly with an increasing concentration of SDS up to CMC. Beyond CMC it increased rapidly and linearly owing to the increase of dodecanol solubility due to the solubilization. Further, from these rate constants and the surface tension *vs.* concentration curve, the diffusion coefficient of dodecanol in water and in aqueous SDS solutions, its solubilization in aqueous SDS solution and the partition coefficient of dodecanol between water and SDS micelles were calculated. Critical micelle concentration of sodium dodecyl sulfate was also determined as a break point of desorption constant *vs.* concentration curve.

The dissolution of and penetration into a monolayer spread on an aqueous surface have been studied by many investigators referring to the state of monolayer or the mechanism of interaction between the monolayer constituents,[1] reaction kinetics of the monolayer,[2] and the mechanism of desorption.[3–5]

In the present report, the mechanism of the rate of dissolution of spread dodecanol monolayer into an underlying aqueous solution of sodium dodecyl sulfate (SDS) was studied by measuring the change of surface tension due to its dissolution. When the rate constant

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[1] J. T. Davies, "Surface Phenomena in Chemistry and Biology," ed. by F. J. Danielli, K. G. A. Pankhurst, and A. C. Riddford, Pergamon Press, London, New York, Paris, Los Angeles (1958), p. 60; D. G. Dervichian, *ibid.*, p. 70.

[2] K. G. A. Pankhurst, *ibid.*, p. 100; M. Muramatsu and H. Sobotka, *J. Colloid Sci.*, **18**, 636 (1963).

[3] L. Saraga, *C. R. Acad. Sic., Paris.*, **233**, 135 (1951).

[4] L. Ter. Minassian-Saraga, *J. Colloid Sci.*, **11**, 398 (1956).

[5] H. L. Rosano and G. Karg, *J. Phys. Chem.*, **63**, 1692 (1959); N. L. Gershfeld and C. S. Patlak, *J. Phys. Chem.*, **70**, 286 (1966); J. T. Davies, *Trans. Faraday Soc.*, **48**, 1052 (1952).

of dissolution was expressed as a function of SDS concentration, two straight lines were obtained which intersected with each other at the critical micelle concentration (CMC) of SDS. Saraga's equation for the monolayer dissolution[3] was extended to explain the rate of dissolution of the monolayer into SDS solution below and above CMC.

Experimental

Materials. Dodecanol used was fractionally distilled and its purity was checked by the gas chromatography to be 98%. It contained no higher homologues. SDS was synthesized by the usual method[6] and was purified by repeated extraction with ether and recrystallization from ethanol until a minimum in the surface tension *vs.* concentration curve disappeared. Benzene used as a spreading solvent was purified by shaking with concentrated sulfuric acid and distilling over sodium hydroxide. Water used as a substrate was purified first by refluxing with an alkaline permanganate solution and then distilling thrice using a Hysil flask.

Apparatus. The Wilhelmy's vertical plate method was adopted for the surface tension measurement. A small displacement of the glass plate due to the change of surface tension was recorded by means of a differential transformer, which was driven by 13 V alternating current input supplied from a 1 kHz oscillator, stabilized by a Zenar diode. The output current from the differential transformer was rectified, properly attenuated, biassed and recorded on a Hitachi QPD recorder. The surface tension change of about 28 dyn/cm could be measured by this apparatus with the error of ±0.14 dyn/cm, when a ground glass plate of 4 cm in perimeter was used.

Procedure. From 5 to 10 μl of benzene solution of dodecanol (5.3×10^{-4} mol/l) was spread from a 50 μl microsyringe on an aqueous surface of SDS solution contained in a glass dish of 7 cm in diameter and 1 cm in depth, and the change in the surface tension was recorded. Typical example of the surface tension change when the benzene solution was spread on the aqueous surface is schematically shown in Fig. 1, where the line AB represents the initial surface tension of the aqueous solution. The surface tension fell to C when the dodecanol solution was spread on the aqueous surface from a single drop at B. The surface tension remained constant from C to D during which period the benzene solution continued to spread, then the surface tension suddenly decreased from D to E and it gradually returned to the value of the substrate solution (AB) as the desorption of dodecanol monolayer proceeded. Five microliter of the spreading solution was confirmed best for the instantaneous completion of the spreading on the aqueous surface. The time required from C to D was a few seconds. So the time for the spreading was negligible compared with the whole period of desorption measurement and the point E was safely taken as the start of the desorption. The evaporation loss during the surface tension measurement was minimized by covering the aqueous surface with a glass plate having a small opening for the passage of the rod attached to the Wilhelmy plate. To facilitate the evaporation of benzene, the monolayer was exposed to open air during the initial period of 30 sec. A special care was taken to ensure the zero contact angle in the advancing meniscus condition. This was confirmed by a slight pushing-down of the plate from an equilibrium position into the solution and checking it to return to the original position when left free.

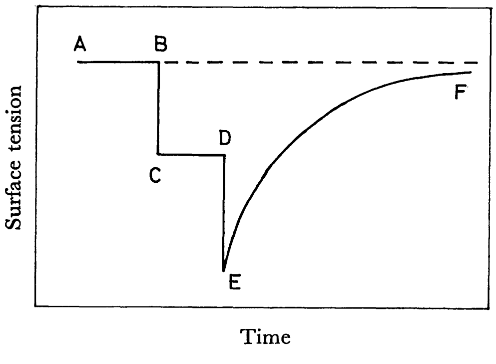

Fig. 1. Surface tension change due to spread benzene.

Results and Discussion

According to the theory proposed by Saraga,[3] a monolayer spread on an aqueous surface partly desorbs to form a sublayer with which the rest of the monolayer establishes a temporary equilibrium, and the rate determining process of desorption is the diffusion of solute from the subsurface through the stagnant layer to the bulk of the solution where the convection current makes the concentration uniform.[7] Thus, the following equation was derived,

$$-\,\mathrm{d}\Gamma/\mathrm{d}t = C(D/\pi t)^{1/2} \tag{1}$$

where Γ expresses the amount of adsorption (mol/cm^2) at time t (sec), C the subsurface concentration of the solute (mol/1000 g) in equilibrium with Γ and D the diffusion coefficient (cm^2/sec). Assuming $C/\Gamma=k$ and $C/F=q$ (F being the surface pressure of the spread monolayer) to be constant throughout the period of desorption, Eq. (1) after integration gives the following relation, which is in accordance with the relation shown experimentally by Roylance.[8]

$$\ln F/F_0 = -\,2k(D/\pi)^{1/2}\cdot t^{1/2} \tag{2}$$

where F_0 is the value of F at $t=0$. Equation (2) predicts a linear relationship between the logarithm of the surface pressure F and the square root of time t. The observed plot of ln F against $t^{1/2}$ for varying concentrations of aqueous SDS substrate is shown in Fig. 2. Here, the difference in surface tension between the aqueous SDS solutions with and without dodecanol monolayer was taken as the surface pressure F of dodecanol monolayer, the assumption being valid for the mixed films containing dodecanol of such low surface pressure as in the present experiment.

In Fig. 2, a good linear relationship was observed to hold between ln F and $t^{1/2}$. The rate constant of desorption was calculated from the slope of these straight lines and plotted against the concentration of SDS as shown in Fig. 3. In this figure, the value of G for lower concentration of SDS in the substrate ($=G_s$) is seen to decrease slightly and linearly from

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[6] E. E. Dreger., *Ind. Eng. Chem.*, **36**, 610 (1944).

[7] J. H. Brooks and A.E. Alexander, *Proc. 3rd Int. Congr. Surface Activity*, Cologne, Vol. 2, 196 (1960).

[8] A. Roylance and T. G. Jones, *Proc. 3rd Int. Congr. Surface Activity*, Cologne, Vol. 2, 123 (1960).

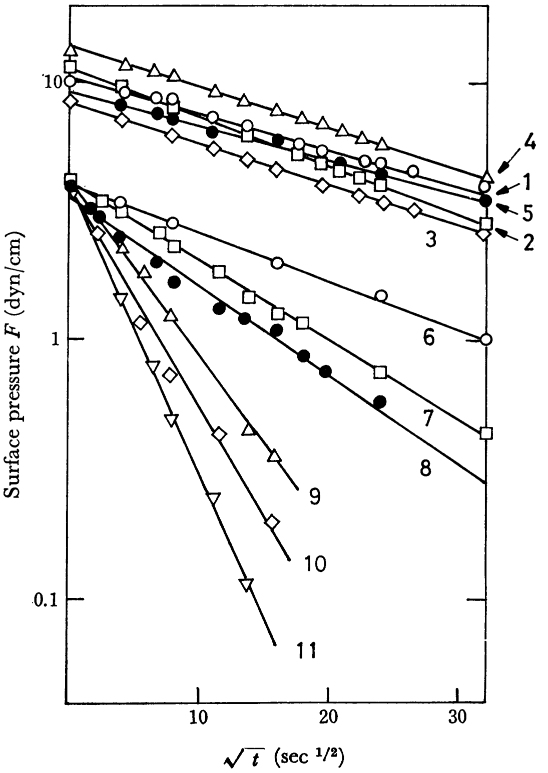

Fig. 2. Surface pressure decrease due to dissolution of surface film.
Conc. of SDS ($\times 10^{-3}$ mol/l)
1; 0 2; 2.52 3; 5.05 4; 6.05
5; 7.05 6; 8.07 7; 9.09 8; 9.51
9; 10.09 10; 12.90 11; 15.35

the value for water up to a point, beyond which G ($=G_m$) increased linearly and steeply with the concentration of SDS. The break point of the curve, 7.7×10^{-3} mol/l, agreed with CMC reported by others.[9] The value of G_s is given by

$$G_s = 2k(D/\pi)^{1/2} \qquad (3)$$

The linear increase of G_m above CMC may reasonably be explained by the solubilization of dodecanol by SDS micelles. According to Eq. (2), the increase of G_m may be due to the increase of k and/or D. However, the solubilization of dodecanol cannot be expected to increase the coefficient of diffusion from the subsurface into the bulk of the solution appreciably, while actual value of $k=C/\Gamma$ is considered to increase to $k'=(C+\Delta C)/\Gamma$, provided that the solubilization equilibrium is instantaneous like surface/subsurface equilibrium. Here, $\Delta C=CC_mPM\times 10^{-3}$ is the increase of dodecanol concentration due to the solubilization, C_m being the concentration of SDS micelles in mol/1000 g water, M the molecular weight of SDS, and P the partition coefficient of dodecanol expressed by

$$\frac{\text{intramicellar concn. of dodecanol (mol/1000 g micelles)}}{\text{intermicellar concn. of dodecanol (mol/1000 g solution)}}$$

Then the following relation holds

$$k' = k(1+C_mPM\times 10^{-3})$$

and Eq. (2) is replaced by

$$\ln F/F_0 = -2k(1+C_mPM\times 10^{-3})(D/\pi)^{1/2}t^{1/2} \qquad (4)$$

where

$$2k(1+C_mPM\times 10^{-3})(D/\pi)^{1/2} = G_m \qquad (5)$$

Equations (4) and (5) well explain the linear relationship above CMC shown in Figs. 2 and 3.

From the Eqs. (3) and (5) we obtain

$$G_m = G_{sm}(1+C_mPM\times 10^{-3}) \qquad (6)$$

Here G_{sm} expresses the value of G_s for SDS solution of critical micelle concentration. According to Eq. (6), P can be calculated from G_{sm} and the slope of G_m *vs.* C_m plot shown in Fig. 3. The value of P thus obtained was 3.62×10^3, which may be compared with similar data obtained for other substances by Herries.[10]

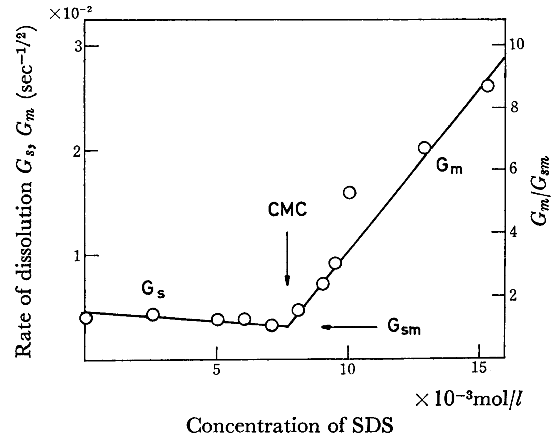

Fig. 3. Rate of dissolution of DOH monolayer into aqueous SDS.

Using this value of P, the amount of solubilization of dodecanol, C_{DOH}, was calculated from the following relation,

$$C_{\text{DOH}} = C_s(1+C_mPM\times 10^{-3}) \qquad (7)$$

where C_s denotes the solubility of dodecanol in the aqueous SDS solution of CMC.

For the measurement of C_s, the solutions were prepared by adding varying amounts of DOH as small volumes of alcoholic solutions to the aqueous SDS solutions of CMC, and the transmittance of the solutions measured at the wave length of 350 mμ was plotted against DOH concentration. The value of C_s was evaluated as the DOH concentration corresponding to the intersection of two straight lines for the transparent and the turbid solutions. $C_s=2.2\times 10^{-4}$ mol/l was obtained at 25°C which is in agreement with the value estimated from the published data,[11] and with the data obtained by surface tension method.[12] Using this value and 7.7×10^{-3} mol/l for the CMC of SDS, C_{DOH} for instance of 7.9×10^{-4} mol/l, for SDS solution of 1×10^{-2} mol/l concentration, was obtained which agrees with 8×10^{-4} mol/l, calculated from the published data.[11,13]

The diffusion coefficients D of DOH in pure water

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[9] H. V. Tartar, *J. Colloid Sci.*, **14**, 115 (1959).

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[11] M. G. Epstein and J. Ross, *J. Phys. Chem.*, **61**, 1578 (1957).

[12] to be published in a near future.

[13] M. Miura and S. Arichi, *J. Sci. Hiroshima Univ.*, **A 22**, 57 (1958).

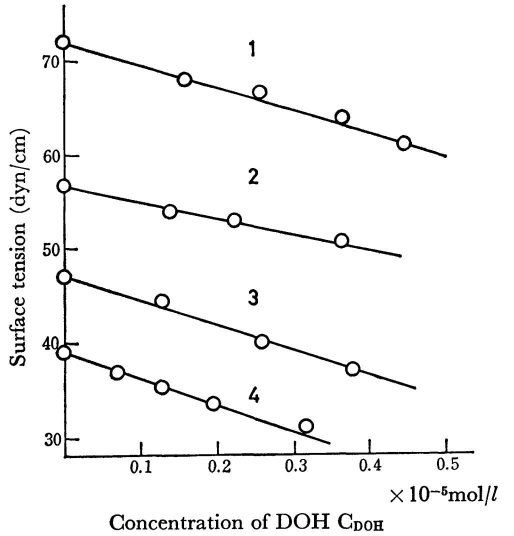

Fig. 4. Surface tension of aq. DOH solution containing SDS. Conc. of SDS ($\times 10^{-3}$ mol/*l*)
1; 0 2; 0.77 3; 4.0 4; 7.7

and in aqueous SDS solution were estimated according to the Eq. (3). For this purpose, the measurements of surface tension σ against concentration C were made for the aqueous solutions of dodecanol containing SDS of a given concentration as shown in Fig. 4, from which k was calculated from the linear part of the curve at sufficiently dilute concentration, by applying the Gibbs adsorption isotherm,

$$1/k = \Gamma/C = -\frac{1}{RT}\frac{d\sigma}{dC}$$

From these values of k and the rate constant G_s for aqueous SDS solution, the diffusion coefficients of 16×10^{-6}, 6.9×10^{-6}, 12×10^{-6}, and 8.4×10^{-6} cm^2 sec^{-1} were obtained for 0, 0.77×10^{-3}, 4.0×10^{-3}, and 7.7×10^{-3} mol/*l* SDS solutions, respectively. Two of these values, especially the value for water, seem too high, presumably due to the evaporation of DOH not being negligible when we consider a fairly small solubility of DOH in pure water. Other values of diffusion constant are considered to be of right order of magnitude, compared with the value for a similar substance.[14]

The authors are grateful to the Ministry of Education for a grant in aid of scientific research.

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[14] F. Van Voorst Vader, Th. F. Erkens, and M. Van Den Tempel, *Trans. Faraday Soc.*, **60**, 1170 (1964).