The Wetting of Paraffin by Aqueous Solutions of Sodium Decyl, Dodecyl and Tetradecyl Sulfates

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The wetting of the surface of such solids as metals, plastics, and fibers by wetting agents and detergent solutions has offered many fundamental problems[1]. However, studies upon the theory underlying the phenomena have hitherto been rather unsatisfactory, especially regarding the relation between the wetting and the solute adsorption[2].

In a previous paper we reported on the relation between the wetting of paraffin by aqueous solutions of fatty alcohol homologues and the solute adsorption[3]. In the present paper we will attempt to study further the relation between the wetting of the paraffin surface by aqueous solutions of sodium decyl, dodecyl and tetradecyl sulfates, and their adsorption.

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[1] A. M. Schwartz, J. M. Perry and J. Berch, "Surface Active Agents and Detergents", Vol. 2, Interscience Publications, New York (1957), p. 543.

[2] K. S. Doss et al., *Proc. Ind. Acad. Sci.*, **7A**, 117 (1938); P. A. Rehbinder et al., *Kolloid-Z.*, **65**, 268 (1933); M. Wada, *Nippon Kogyo Kaishi*, **59**, 681 (1943).

[3] T. Tsunoda, This Bulletin, **36**, 445 (1963).

Experimental

The detergents used were sodium decyl (SDeS), dodecyl (SDoS) and tetradecyl (STS) sulfates. They were prepared by the reaction of corresponding alcohols with chlorosulfonic acid in ether. In order to purify them, the alkyl sulfates obtained were dissolved in ethyl alcohol, treated with charcoal, and then recrystallized. The disappearance of the minimum in surface tension concentration curves, as is shown in Fig. 1, proved their purity. The paraffin used was purified by treating it with concentrated sulfuric acid, then with sodium hydroxide, and finally by vacuum distillation. For the wettability measurement, the paraffin surface was prepared as a thin layer on a glass rod of a uniform diameter. The measurements of wettability and surface tension were made in the same manner as was reported in a preceding paper[3]. The temperature was controlled at 30±0.3°C throughout the experiments. No particular control of the pH was made for the solution used. It was about 6.

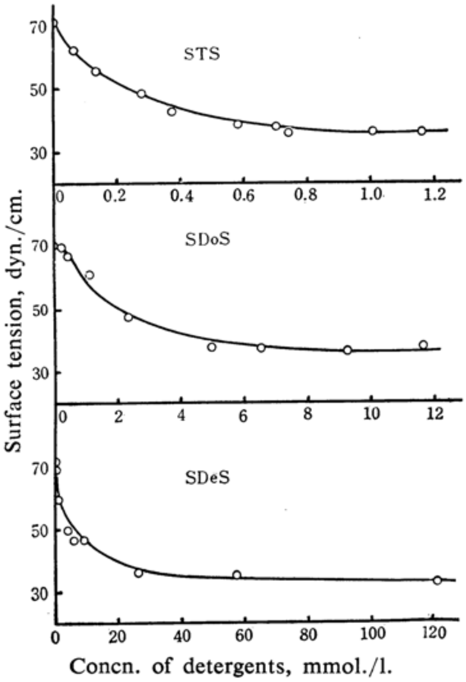

Fig. 1. Surface tension vs. concentration of detergents.

Results and Discussion

The changes in the wetting tension of paraffin towards aqueous solutions of detergents with the time of immersion in those solutions are shown in Fig. 2, for instance, for SDoS solution, where $\sigma_1 \cos\theta_r$ is the wetting tensinon, σ_1, the surface tension of the solution, and θ_r, the receding contact angle of the solution on paraffin. The equilibrium values of the wettability were attained within 60 min. after the immersion of the paraffin into the detergent solutions. The equilibrium advancing and receding contact angles thus obtained were plotted against the concentration of detergent solutions as shown in Figs. 3, 4 and 5. The hysteresis of the contact angles was at

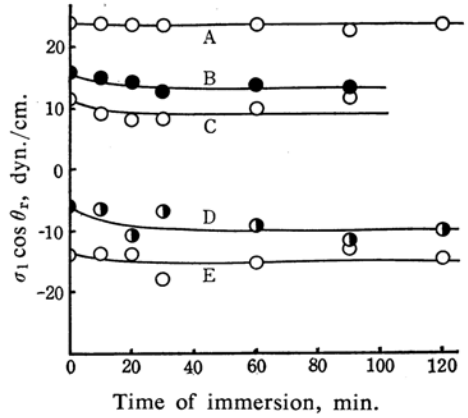

Fig. 2. $\sigma_1 \cos\theta_r$ vs. time of immersion into SDoS solution.

A 2.36×10^{-3} mol./l.
B 9.32×10^{-3}
C 1.57×10^{-2}
D 1.15×10^{-3}
E 2.70×10^{-4}

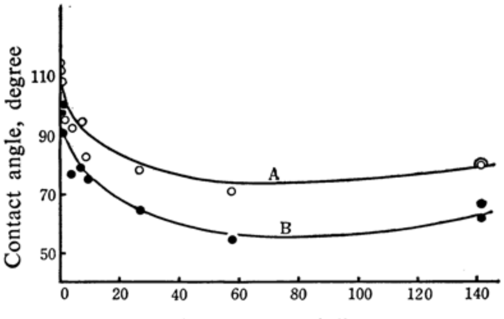

Fig. 3. Contact angle vs. concentration of SDeS.

A, advancing B, receding

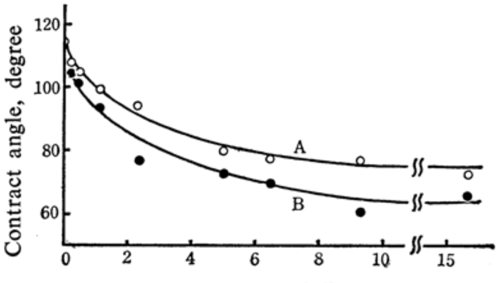

Fig. 4. Contact angle vs. concentration of SDoS.

A, advancing B, receding

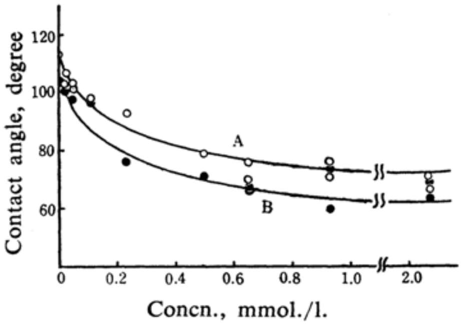

Fig. 5. Contact angle vs. concentration of STS.
A, advancing B, receeding

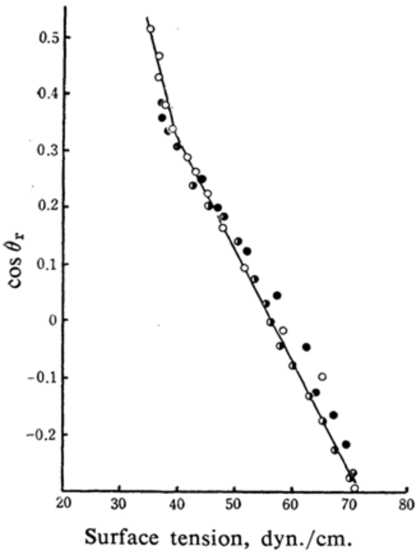

Fig. 6. $\cos\theta_r$ vs. surface tension.

○ Sodium decyl sulfate
● Sodium dodecyl sulfate
◑ Sodium tetradecyl sulfate

most 10 degrees in these experiments. Figure 6 shows the relation between the cosine of the receding contact angles and the surface tension of the detergent solutions. We can observe in this figure that the curves tend to show a discontinuity in slope at about 40 dyn./cm. A similar phenomenon was observed for the wetting of teflon and polyethylene by several detergent solutions[4]. We calculated the Zisman critical surface tension, γ_c[5], by the extrapolation of the σ_1 vs. $\cos\theta_r$ plot to $\cos\theta_r=1$ and thus found γ_c to be 26 dyn./cm.

Now we shall refer to the wetting isotherm. As in a preceding paper[6] we used the following wetting isotherm;

$$\cos\theta_r=\frac{\sigma_1+\sigma_w}{\sigma_1}(\phi+K\Gamma)-1 \tag{1}$$

where θ_r denotes the receding contact angles, σ_1 and σ_w, the surface tension of the solution and solvent (water) respectively, Γ, the amounts of solute adsorption in mol./cm^2, and ϕ and K constants. In order to check our wetting isotherm 1, we calculated Γ using Gibbs' adsorption isotherm:

$$\Gamma=\frac{\mathrm{d}(\sigma_1\cos\theta_a)}{\boldsymbol{RT}\,\mathrm{d}\ln c} \tag{2}$$

and made plots between the Γ thus obtained and $\sigma_1(\cos\theta_r+1)/(\sigma_1+\sigma_w)$, as in the preceding paper[3]. Figures 7, 8 and 9 show the adsorption isotherm $\Gamma\sim c$. In the region of concentration lower than the CMC of the detergents, the apparent maximum in the adsorption isotherm is observed in these curves. It is, however, hard to interpret these maxima in the adsorption isotherm, since the $\sigma_1\cos\theta_a\sim\ln c$ plot is not generally so accurate in the concentrated region of saturated adsorption. Figure 10 shows the $\sigma_1(\cos\theta_r+1)/(\sigma_1+\sigma_w))\sim\Gamma$ plots. The plots indicate a linear relation in the

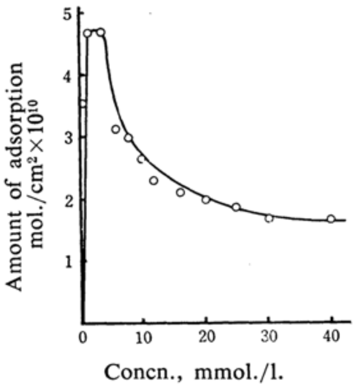

Fig. 7. Adsorption isotherm of SDeS for paraffin/solution interface.

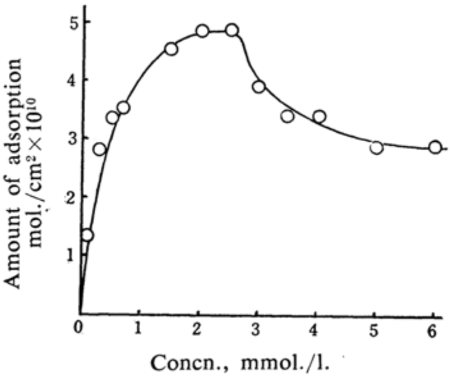

Fig. 8. Adsorption isotherm of SDoS for paraffin/solution interface.

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[4] W. A. Zisman et al., *J. Phys. Chem.*, **63**, 1241 (1959).
[5] W. A. Zisman et al., *J. Colloid Sci.*, **47**, 428 (1952).
[6] T. Sasaki, H. Kumanomido and T. Tsunoda, 2nd International Congress of Surface Activity, III, Butterworths, London (1957), p. 153.

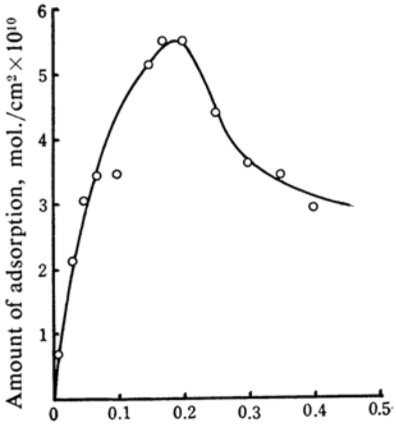


Fig. 9. Adsorption isotherm of STS for paraffin/solution interface.

region of concentration less than that of the maximum adsorption. From this linearity we calculated the constants ϕ and K, which are shown in Table I. In this table we may notice, that the calculated values of ϕ are constant, regardless of the detergents used, while the K values decrease with the increasing molecular weight. These results are similar with the values of ϕ and K obtained for fatty alcohols on paraffin³⁾. Inserting the values of ϕ and K into Eq. 1, we obtained:

$$\left.\begin{aligned}
&\text{for SDeS}\\
&\cos\theta_r=\frac{\sigma_1+\sigma_w}{\sigma_1}(0.353+0.026\times10^{10}\Gamma)-1\\
&\text{for SDoS}\\
&\cos\theta_r=\frac{\sigma_1+\sigma_w}{\sigma_1}(0.347+0.025\times10^{10}\Gamma)-1\\
&\text{for STS}\\
&\cos\theta_r=\frac{\sigma_1+\sigma_w}{\sigma_1}(0.347+0.016\times10^{10}\Gamma)-1
\end{aligned}\right\}\quad(3)$$

Figure 11 shows the comparison between the values obtained from Eq. 3 (solid line) and the observed values (circles). Beyond the concentration of maximum adsorption of detergents, the discrepancies between the calculated and observed contact angle values are marked in all cases, partly because of the inevitable inacuracy in observation already mentioned.

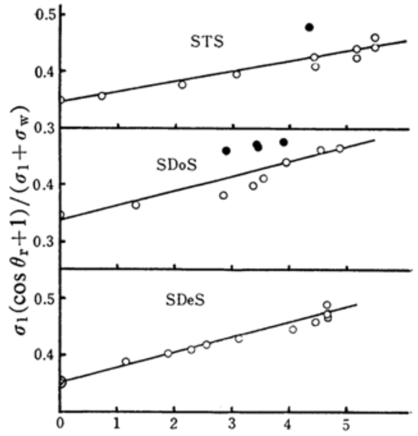
TABLE I. CONSTANTS ϕ AND K IN WETTING ISOTHERM 1

Detergent	ϕ	K, cm²/mol.
Sodium decyl sulfate	0.353	2.6×10^8
Sodium dodecyl sulfate	0.347	2.5×10^8
Sodium tetradecyl sulfate	0.347	1.6×10^8

In Figs. 12, 13 and 14, we show $F\sim A$ diagram, together with the $FA\sim A$ curves inserted. The surface pressure of the adsorbed film on the solid/solution interface, F, and the area occupied by molecules in the film, A, is obtained in a manner similar to that used in a preceding paper⁶⁾. Applying Volmer's equation, $FA=ikT+A_0F$ to the $FA\sim F$ curves, as shown by solid lines in Figs. 12, 13 and 14, the co-area A_0's are obtained as 30, 23, 30 Å²/molec. for SDeS, SDoS and STS respectively.

We further examined the validity of Traube's rule, which is expressed by:

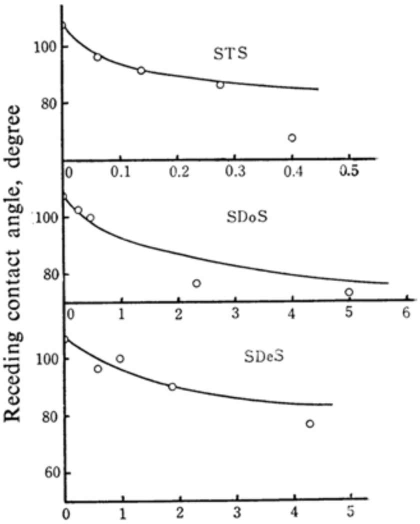
$$\ln (F/c)_n=\ln (F/c)_1+\Delta w(n-1)/\boldsymbol{RT} \qquad (4)$$



Amount of adsorption, mol./cm² × 10¹⁰

Fig. 10. Validity of Eq. 1.

○ Concn. less than max. adsorption
● Concn. beyond max. adsorption



Concn., mmol./l.

Fig. 11. Comparison between calculated (solid line) and observed (circle) contact angles.

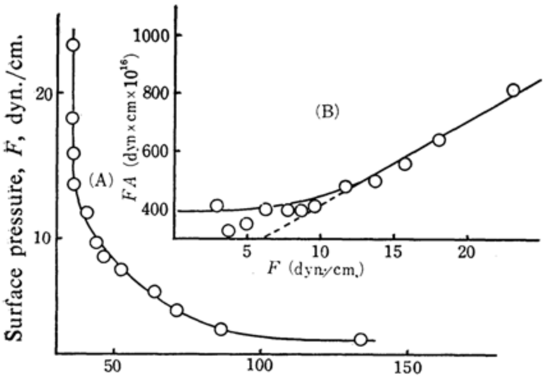


Fig. 12. (A) Pressure∼area and (B) $FA\sim F$ relations for adsorbed film of SDeS for paraffin/solution interface.

where F/c denotes the slope of the $F\sim c$ curve at $c=0$, n, the number of carbon atoms in the alkyl sulfate molecules, and Δw, the work per CH_2 of adsorbed solute molecule required to bring it from the paraffin surface back into the interior of the solution. Figure 15 shows the lineality between ln (F/c) and n. From these figures, we obtained 588.9 cal./mol. CH_2 as the Δw for the paraffin/solution interface. This figure is smaller than 824 cal./mol. CH_2 obtained for the fatty alcohol at the solution/paraffin interface[3]. For the air/solution interface, we obtained 534.7 cal./mol. CH_2 as the Δw value. This value is also smaller than that of 656 cal./mol. CH_2 for fatty alcohols at the aqueous alcohol solution surface[3].

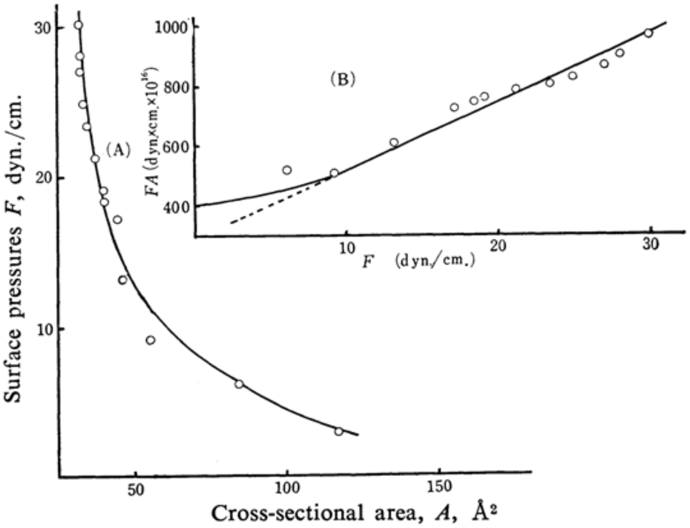


Fig. 13. (A) Pressure∼area and (B) $FA\sim F$ relations for adsorbed film of SDoS for paraffin/solution interface.

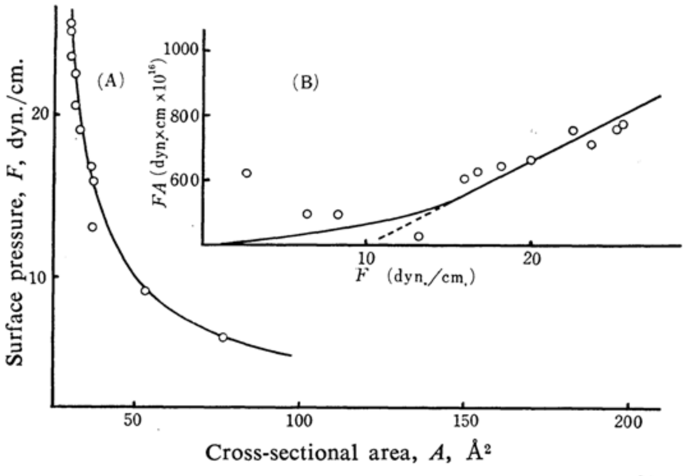


Fig. 14. (A) Pressure∼area and (B) $FA\sim F$ relations for adsorbed film of STS for paraffin/solution interface.

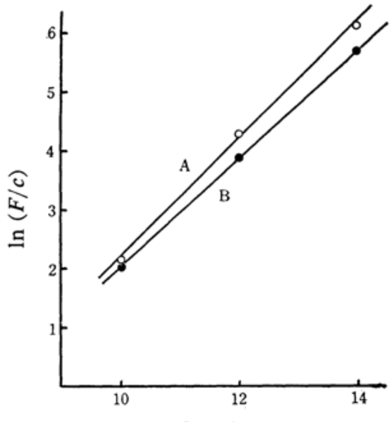


Fig. 15. ln (F/c) vs. number of carbon atoms of detergent molecules

A Paraffin/solution interface
B Air/solution interface

Summary

The wettability of the paraffin by aqueous solutions of sodium decyl, dodecyl and tetradecyl sulfate have been studied. A slight but distinct discontinuity of the slope in the curve of the cosine of the receding contact angle vs. the surface tension of the solution was observed for the solution of sodium decyl, dodecyl and tetradecyl sulfate. The discontinuity of the slope appeared at the surface tension of about 40 dyn./cm. It was found that the wetting isotherm which had been proposed by the present author, and which had been found valid for the wetting of paraffin by the aqueous solution of fatty alcohol homologues, was also valid for this experiment in the dilute aqueous solution of sodium alkyl sulfates. The adsorption energy was 588.9 cal./mol. CH_2 and 534.7 cal./mol. for the paraffin/solution and air/solution interfaces respectively.

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