The Wetting of Paraffin by Aqueous Solutions of Fatty Alcohol Homologues

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The relation between the wetting of a solid by solutions and the adsorption of the solute has been studied by various authors. Rehbinder[1] and Cook[2] have proposed formulas expressing the relation between contact angle and adsorption, but these are largely empirical in nature and lack theoretical foundation. On the other hand, Doss[3] and Wada[4] have derived theoretical formulas, but these are not always applicable to all of the practical cases. Recently, Bartell[5] has given a wetting isotherm which predicted fairly well the relation between the solute adsorption and the adhesion tension in the case of the wetting of platinum by water. His formula, however, concerns hydrophilic surfaces and is not applicable to hydrophobic surfaces such as paraffin, which, according to his formula, should have a portion of the surface free from any adsorption, at least in the case of wetting by pure water, which is different from the adsorption model he assumed.

We have also attempted to derive an equation based on the molecular structure of the adsorbed layer which was valid both for the wetting and the anti-wetting of a solid surface by aqueous ethyl alcohol and xanthate solutions respectively[6]. The present investigation was undertaken further to check our wetting isotherm for the case of the wetting of paraffin by aqueous solutions of alcohol homologues and to obtain further knowledge concerning adsorbed films on solid surfaces.

Experimental

The alcohols used were *n*-propyl, *n*-butyl, *n*-amyl and *n*-octyl alcohols, which had been refluxed over calcium oxide for several hours and then distilled twice before use. Their boiling points were within the range of 1°C of the published data. 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 by dipping a glass rod of a uniform diameter into molten paraffin, withdrawing it, and then solidifying the paraffin film on the rod in air. The surface thus obtained was sufficiently smooth for the measurement of contact angle not to obscure the conclusion obtained. The contact angle and surface tension were measured using the Wilhelmy balance. The temperature was controlled to 25 ± 0.3°C throughout the experiments.

Results and Discussion

Contact Angles.—The changes in contact angle with time of immersion in an alcohol solution are shown in Table I, which shows a nearly constant value of the angle after an hour. As the time dependence of the surface tension of aqueous alcohol solutions was not perceptible in this experiment, the observed change in the contact angle may be ascribed mainly to a slow change in the solid/solution interfacial tension with time. In the present experiment, contact angles were measured for paraffin soon after it had been immersed in solution for one hour. The advancing and receding contact angles thus obtained were

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[1] P. A. Rehbinder et al., *Kolloid-Z.*, **65**, 268 (1933).

[2] M. A. Cook et al., *J. Phys. Colloid Chem.*, **55**, 1219 (1951).

[3] K. S. Doss et al., *Proc. Ind. Acad. Sci.*, **7A**, 117 (1938).

[4] M. Wada, *Nippon Kogyo Kaishi*, **59**, 681 (1943).

[5] L. S. Bartell et al., *J. Phys. Chem.*, **64**, 513 (1960).

[6] T. Sasaki, H. Kumanomido and T. Tsunoda, 2nd International Congress of Surface Activity, III, Butterworths, London (1957), p. 153.

TABLE I. THE CHANGES OF CONTACT ANGLE WITH TIME OF IMMERSION IN ALCOHOL SOLUTIONS

Alcohol	σ dyn./cm.	$t=0$		$t=30$		$t=60$	
		θ_a	θ_r	θ_a	θ_r	θ_a	θ_r
n-Propyl alc.	60.4	109.8	101.4	110.4	110.6	109.6	98.6
n-Butyl alc.	62.0	112.7	91.8	109.2	90.5	108.9	90.0
n-Amyl alc.	62.0	110.7	97.1	96.2	95.5	95.5	94.8
n-Octyl alc.	60.4	109.7	98.2	110.0	97.8	109.2	97.1

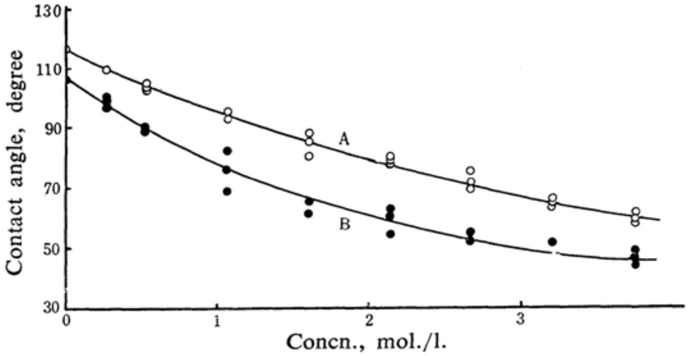

Fig. 1. Contact angle vs. concentration of *n*-propyl alcohol.
A, advancing B, receding

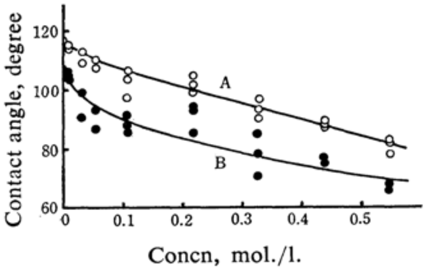

Fig. 2. Contact angle vs. concentration of *n*-butyl alcohol.
A, advancing B, receding

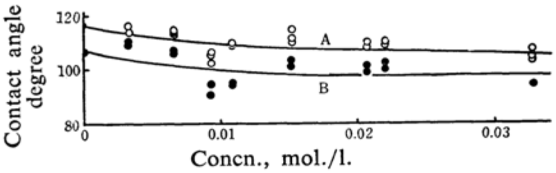

Fig. 3. Contact angle vs. concentration of *n*-amyl alcohol.
A, advancing B, receding

plotted against the concentration of solutions, as is shown in Figs. 1, 2, 3 and 4. It was found that the hysteresis of the contact angles was at most about 10 degrees throughout the experiments.

Wetting Isotherm.—As for the wetting isotherms, Doss3) proposed an equation which gave the relation between the contact angle and the liquid adsorption as:

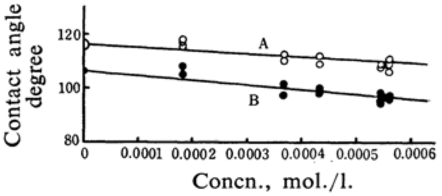

Fig. 4. Contact angle vs. concentration of *n*-octyl alcohol.
A, advancing B, receding

$$\cos\theta = 2\phi - 1 \tag{1}$$

where θ denotes the contact angles of pure liquid and ϕ, the fractional area of liquid adsorption. By a similar reasoning we derived a more general isotherm6) for the wetting of a solid by solution:

$$\cos\theta_r = \frac{\sigma_1 + \sigma_w}{\sigma_1}(\phi + aX) - 1 \tag{2}$$

where θ_r denotes a receding contact angle, σ_1 and σ_w the surface tension of the wetting solution and solvent (water) respectively, ϕ and a, constants depending on the nature of the wetting solution (namely solvent and solute), and X, the fraction of the surface covered with the solute molecules. In deriving Eq. 2 we used θ_r for the contact angles which corresponded to the work of adhesion, $W_a = \sigma_1(\cos\theta_r + 1)$, instead of $W'_a = \pi + \sigma_1(\cos\theta_a + 1)$ for the advancing contact angle, θ_a, where π denotes the spreading pressure of the adsorbed film on the solid. Equation 2 can be reduced to the Doss Eq. 1 in the case of a pure liquid where $X=0$, $\sigma_1=\sigma_w$. Now in Eq. 2, we can put $X=\Gamma\lambda$, where Γ denotes the amount of adsorption in mol./cm², and λ the area occupied by a mole of an adsorbed substance in a closely packed state in cm²/mol. Equation 2 then takes the form:

$$\cos\theta_r=\frac{\sigma_1+\sigma_w}{\sigma_1}(\phi+K\Gamma)-1 \qquad (3)$$

where K is a new constant equal to $a\lambda$. We checked our wetting isotherm Eq. 3 using the experimental values of σ_r, σ_w, σ_1 and Γ. Γ is calculated from the Gibbs' adsorption isotherm:

$$\Gamma=\frac{\mathrm{d}(\sigma_1\cos\sigma_a)}{\boldsymbol{RT}\,\mathrm{d}\ln c} \qquad (4)$$

where c expresses the concentration in mol./l. of alcohol in the wetting solution. We used the advancing contact angle, θ_a, for the calculation of Γ, because in the advancing liquid state the solid surface is considered to be practically free from adsorbed solute, which is also assumed to be the case in the derivation of Eq. 4. The adsorption isotherms thus obtained for the paraffin/aqueous solution interface, together with those for the aqueous solution surface, are shown in Figs. 5 and 6. We can see in these figures that the amount of adsorption is somewhat larger for the paraffin/solution interface than for the aqueous surface, while it is nealy equal for both surfaces in the case of butyl and amyl alcohols and is a little larger for the paraffin/solution interface in the case of octyl alcohol. Davies[7] reported that the proportionality between Γ and the concentration of solute is better for the oil/solution interface than for the aqueous surface. However, we can observe no such differences.

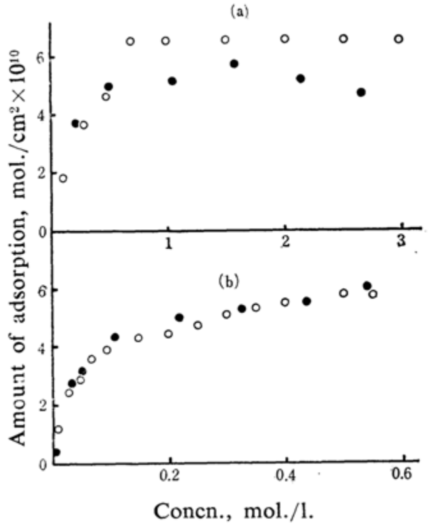

Fig. 5. Adsorption isotherms of (a) *n*-propyl and (b) *n*-butyl alcohol on paraffin/solution (○) and air/solution (●) interfaces.

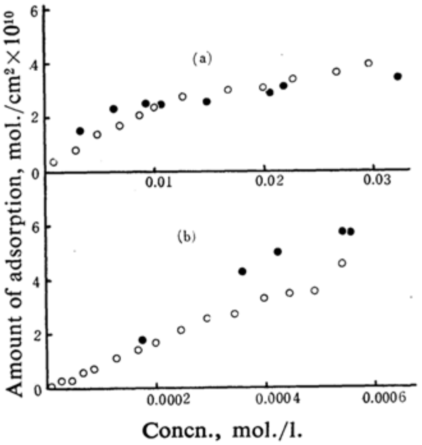

Fig. 6. Adsorption isotherms of (a) *n*-amyl and (b) *n*-octyl alcohol on paraffin/solution (○) and air/solution (●) interfaces.

In order to check Eq. 3, it was transformed into

$$\frac{\sigma_1(\cos\theta_r+1)}{\sigma_1+\sigma_w}=\phi+\boldsymbol{k}\Gamma \qquad (5)$$

and $\sigma_1(\cos\theta_r+1)/(\sigma_1+\sigma_w)$ was plotted against Γ. The results are shown in Fig. 7. The

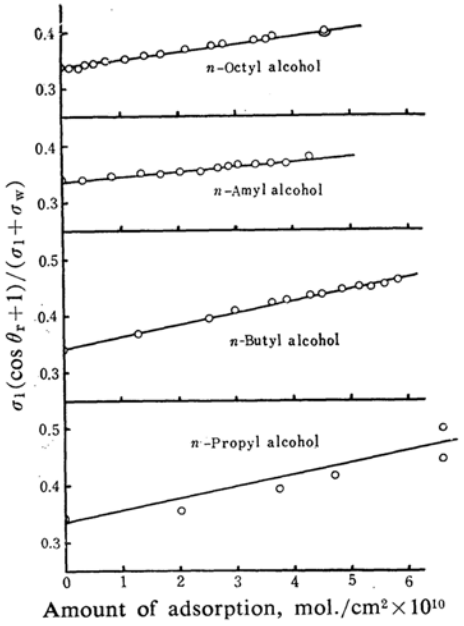

Fig. 7. Validity of Eq. 3.

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[7] J. T. Davies, *Proc. Roy. Soc.*, **A245**, 415 (1958).

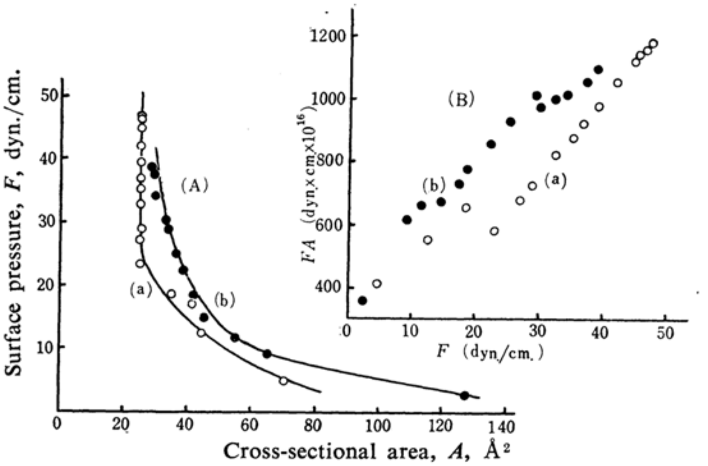

Fig. 8. (A) Pressure∼area and (B) $FA\sim F$ relations for adsorbed films of (a) *n*-propyl and (b) *n*-butyl alcohol on paraffin surface.

linearity obtained in these figures lends support to the validity of Eqs. 2 and 3. From the linearity, we calculated the ϕ and K constants which are shown in Table II. We can see in Table II that the calculated value of ϕ is constant, regardless of the alcohol used, while the values of K decrease with an increase in molecular weight with the exception of the irregular value for amyl alcohol. The value of ϕ, which is the proportion of polar part to the total area of the solid surface, should be practically independent of the nature of alcohol used. That the value of ϕ is 0.34 means that the polar part of the surface is about one-third of the total area of the solid surface. The K value, on the other hand, may be expected to decrease with an increase in the molecular weight of the solute, since it depends on the relative polarity of solute and is expected to decrease with an increase in the molecular weight. This requirement is also satisfied as a whole. Using the adsorption isotherm of the Langmuir type, c was substituted for Γ in Eq. 3. We thus obtained, for *n*-propyl alcohol:

$$\cos\theta_r=\frac{\sigma_l+\sigma_w}{\sigma_l}\left(0.346+\frac{c}{1+6.82c}\right)-1$$

for *n*-butyl alcohol

$$\cos\theta_r=\frac{\sigma_l+\sigma_w}{\sigma_l}\left(0.347+\frac{c}{0.536+8.11c}\right)-1$$

for *n*-amyl alcohol

$$\cos\theta_r=\frac{\sigma_l+\sigma_w}{\sigma_l}\left(0.339+\frac{c}{0.34+19.6c}\right)-1 \tag{6}$$

for *n*-octyl alcohol

$$\cos\theta_r=\frac{\sigma_l+\sigma_w}{\sigma_l}\left(0.342+\frac{c}{7.88\times10^{-3}+5.58c}\right)-1$$

TABLE II. CONSTANTS ϕ AND K IN WETTING ISOTHERM 3

Alcohol	ϕ	K, cm²/mol.
n-Propyl alc.	0.346	2.2×10^8
n-Butyl alc.	0.347	1.9×10^8
n-Amyl alc.	0.339	0.8×10^8
n-Octyl alc.	0.342	1.2×10^8

The Eqs. 6 are shown as solid lines in Figs. 1—4. We can further express the surface tension, σ_l of the Eqs. 6 in terms of the concentration, c, using an equation, for instance, of the Szyzkowski type, and express the contact angle as a function of the solute concentration alone, but we did not attempt to do so. It should be noted that the wetting phenomena is characterized both by the wetting power (K) of the liquid and the wettability (ϕ) of the solid surface, besides the surface tension of the liquid and the amount of solute adsorption.

The Equation of State for the Film at the Solid/Solution Interface.—Although a number of studies have been undertaken concerning the equation of the state of the film at the liquid/air interface[8], only a few have been reported on the solid/liquid interface[9]. The surface pressure, F, of the adsorbed film at the aqueous solution/solid interface can be expressed by:

$$F\equiv\sigma_{l_o}-\sigma_l=\sigma\cos\theta_a-\sigma_o\cos\theta_{a_o} \tag{7}$$

where σ_{l_o} and σ_l denote the solid/water and solid/solution interfacial tensions, σ_o and σ, the surface tensions of water and the aqueous solution, and θ_{a_o} and θ_a, the advancing contact angles of water and the aqueous solution on

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[8] N. K. Adam, "Physics and Chemistry of Surfaces", Oxford University Press, London (1938), p. 115.

[9] W. D. Harkins et al., *J. Am. Chem. Soc.*, **62**, 3377 (1940).

TABLE III. CROSS-SECTIONAL AREA OF ALCOHOL MOLECULE

Alcohol	from Volmer Eq.	from Langmuir Eq.
n-Propyl alc.	25.0 (Å²/mol.)	24.9 (Å²/mol.)
n-Butyl alc.	24.0 (Å²/mol.)	25.0 (Å²/mol.)
n-Amyl alc.	24.0 (Å²/mol.)	26.6 (Å²/mol.)
n-Octyl alc.	—	11.6 (Å²/mol.)

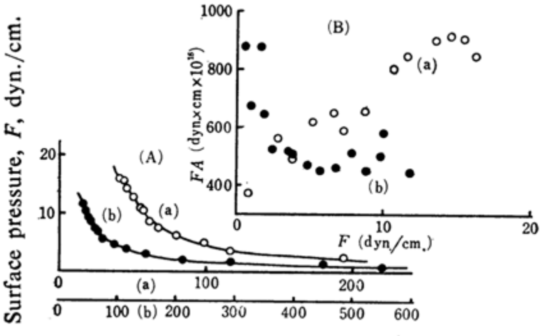

Fig. 9. (A) Pressure∼area and (B) $FA\sim F$ relations for adsorbed films of (a) *n*-amyl and (b) *n*-octyl alcohol on paraffin surface.

the solid respectively. Thus, we can calculate the surface pressure of the film at the solid/liquid interface from the measurement of the surface tension and contact angle. Further, the area occupied by a molecule in the film is given by

$$A=1/\Gamma N \tag{8}$$

where N denotes the Avogadro number. The $F\sim A$ diagrams were then constructed as shown in Figs. 8 and 9, with $FA\sim F$ curves inserted. The $FA\sim F$ curves of *n*-propyl, *n*-butyl and *n*-amyl alcohols can then be expressed by Volmer's equation as:

$$FA=ikT+A_0F \quad \text{or} \quad F(A-A_0)=ikT \tag{9}$$

where i and the co-area A_0 are constants. The slope of the straight line of $FA\sim F$ gives the co-area of the adsorbed molecule which corresponds to the saturation amount of adsorption obtained from Langmuir's formula. These values are shown in Table III. The two values coincide and are also equal to the corresponding values of the air/water interface.

Traube's Rule for the Solid Solution Interface.—Traube's rule[10] predicts that

$$\ln(F/c)_n=E+\frac{\Delta W}{RT}n \tag{10}$$

where $(F/c)_n$ denotes the slope of $F\sim c$ curve at its origin for aqueous C_n-alcohol, ΔW, the work per mol. of CH_2 chain of the alcohol

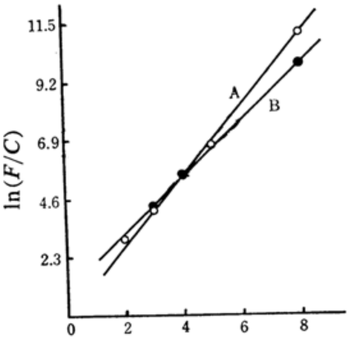

Fig. 10. $\ln(F/c)_n$ vs. number of carbon atoms of fatty alcohol homologues.
A, Paraffin/solution interface
B, Air/solution interface

molecules required to bring it from the adsorbed layer to the interior of the solution, and E, a constant. To check Eq. 10, the value of $(F/c)_n$ was calculated from the slope of the $F\sim c$ curve (not shown) at the origin for each solution of alcohol homologues. The diagram of $\ln(F/c)_n$ thus obtained against n is shown in Fig. 10, together with the diagram for an aqueous solution for purposes of comparison. In this figure the plot for ethanol was taken from a preceding report⁶⁾. As is shown in Fig. 10, the linear relation of Eq. 10 holds for both paraffin/solution and air/solution interfaces. We evaluated ΔW from this slope, obtaining the values of 824 cal./mol. CH_2 for the paraffin/solution interface and 656 cal./mol. CH_2 for the aqueous solution surface respectively. As for the ΔW of the paraffin/solution interface, we obtained 774 cal./mol. CH_2 for saturated fatty acid adsorbed on paraffin[11], 1000 cal./mol. CH_2 from the experiment of monolayer penetration[12], 800 cal./mol. CH_2 from the adsorption of benzylamine on the α-bromopalmitic acid monolayer[13], and 810 cal./mol. CH_2 for the oil/solution interface[14], while for the ΔW of the air/solution interface, values of 630 cal./mol.[14] and 640 cal./mol.[12] are given. Our ΔW values may be considered to be of the right order of magnitude as compared with these published

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[10] J. T. Davies and E. K. Rideal, "Interfacial Phenomena", Academic Press, New York (1961), p. 155.

[11] H. Gastalla, *Compt. rend.*, **235**, 941 (1952).

[12] K. G. A. Pankhurst, *Proc. Roy. Soc.*, **A179**, 393 (1942).

[13] D. J. Crisp, "Surface Chemistry", Butterworths, London (1949), p. 65.

[14] J. T. Davies, *Trans. Faraday Soc.*, **48**, 1052 (1952).

data. As is seen, the value of ΔW for the paraffin/solution interface is somewhat larger than that for the air/solution interface. This is consistent with the view of a larger affinity of the hydrocarbon chain of the alcohol molecule for the paraffin/solution interface than for the air/solution interface[14].

Here we may add that, in the present case, Eq. 4 or its integrated form,

$$\sigma_1 \cos \theta_a = \boldsymbol{RT} \int_0^c \Gamma \, \mathrm{d} \ln c$$

can also be considered as a wetting isotherm which, if we put Γ as a Langmuir-type adsorption isotherm, can be integrated to give an adsorption isotherm similar to that of Eq. 3. However, we should like to emphasize that Eq. 3 is more useful than Eq. 4 because (i) Eq. 3 is an integrated formula with respect to Γ, while the integration of Eq. 4 is not always possible, (ii) Eq. 4 is limited only to cases of physical adsorption, as in the present case, while Eq. 3 fits the wetting data even when Eq. 4 fails to explain the adsorption, as in the case of the chemisorption of xanthate on a mineral surface[6] or the surface attack of polystyrene by sulfuric acid[15], and (iii) Eq. 3 offers the more distinct molecular explanation of the effect of surface film on wetting. It should also be added that Eqs. 3 and 4 cannot be applied to the cases of polymolecular adsorption or deep surface chemical attack where the wetting property cannot be considered as a simple function of the adsorption amount.

Summary

The wettability of paraffin towards aqueous solutions of *n*-propyl, *n*-butyl, *n*-amyl and *n*-octyl alcohols has been studied. It has been found that the wetting isotherm which had been proposed by the present author and had been valid for the wetting of paraffin by an aqueous ethyl alcohol solution, could also be applied successfully to the present systems. The equations of state for the adsorbed films of these alcohols at the paraffin/aqueous solution interface were obtained. It was further shown that Traube's rule holds for the paraffin/aqueous alcohol solution interface as well as for the air/solution interface. The adsorption energies found were 824 cal./mol.$\cdot$ CH_2 for the paraffin/solution interface and 656 cal./mol. CH_2 for the aqueous surface.

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[15] T. Tsunoda, T. Seimiya and T. Sasaki, This Bulletin, 35, 1570 (1962).