The Theory of the Adsorption Monolayer with Lateral Intermolecular Interaction and Its Application to Aqueous Alcohol Solutions

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A theoretical relation between the fractional adsorption amount, θ, and the concentration, C, taking account of the lateral interaction between the adsorbed molecules is used to integrate the Gibbs equation, and the relation between the surface pressure, F, and the molecular area, A, is derived. Since the equation does not contain the parameter, k_0, related to the strength of adsorption, it is concluded that there is no substantial difference between the adsorption monolayers and the insoluble monolayers. The relation between F and C is also derived and compared with the experimental data for normal alcohols. The standard affinity of adsorption, $-\Delta\mu^0$, and the energy of lateral interaction, ε, increased linearly with the number of carbon atoms of the alcohols, n. Finally, it has been shown that the experimental data can be explained well with the theoretical equation presented here, but not with Szyszkowski's, the latter being derived for negligible lateral interaction.

The energy or free energy of adsorption from a solution to its surface has been discussed for many years in connection with the surface activity of various substances, but not much attention has been paid to the lateral interaction between solute molecules in the adsorption monolayers. This interaction, however, seems to be important because the adsorption monolayers seem to fairly compact in ordinary concentration ranges.

The behavior of the adsorption monolayer could not be discussed hitherto in enough detail so that the effect of the lateral interaction could be detected. This is because some ambiguity is introduced when the experimental relation between the surface tension of a solution and the concentration of the surface-active solute is differentiated, graphically or numerically, in order to use the Gibbs differential equation in the determination of the adsorption amount or the molecular area in the adsorption monolayer.

In the present paper, theoretical equations will be derived for the adsorption monolayer with lateral intermolecular interaction. A method will be proposed to determine the values of the parameters which are used in the equations. Finally, the method will be applied to aqueous normal alcohol solutions and the parameter values thus obtained will be discussed.

Theoretical

Adsorption Equation of Interacting Molecules. Adsorption isotherms of surface active substances at the surfaces of their own solutions are often expressed by the Langmuir equation. This is in accord with the well-known fact that the surface tension of such a solution as a function of the concentration is expressed by the empirical Szyszkowski equation, because the latter equation can be derived theoretically when the Gibbs adsorption equation is integrated with the Langmuir equation if the solute is a nonelectrolyte at a dilute concentration, so the activity coefficient is assumed to be independent of the concentration.[1)]

The Langmuir equation takes the size of the adsorbed molecules, or the repulsion by steric hindrance, into account, but it does not take the lateral cohension between adsorbed molecules into account, since the equation was originally derived from the idea of site adsorption. If the lateral interaction is taken into consideration, the chemical potential of the solute in such an adsorption monolayer, μ, is taken to be different from that of the Langmuir monolayer, μ_L, by $\Delta\mu_{int}$:

$$\mu = \mu_L + \Delta\mu_{int}. \tag{1}$$

Since the probability of a molecule existing next to a given molecule may be assumed to be equal to the fractional adsorption amount, θ, the interaction energy in the monolayer is proportional to θn; therefore,

$$\Delta\mu_{int} = \frac{\partial}{\partial n}\left(-\frac{\varepsilon}{2}\theta n\right) = -\varepsilon\theta, \tag{2}$$

where ε is the energy of lateral interaction and

$$\theta = n/n_0 = \Gamma/\Gamma_0 = A_0/A. \tag{3}$$

Here, n is the moles of the adsorbed solute, Γ is the adsorption amount per unit area, A is the area occupied by one molecule, and the values with the 0 subscript are for the saturated adsorption.

At the adsorption equilibrium, μ is equal to the chemical potential of the solute in the solution, μ_S, which is given by the following equation if the activity coefficient is assumed to be independent of the concentration, C:

$$\mu_S = \mu_S^0 + RT\ln C, \tag{4}$$

where μ_S^0 is the standard chemical potential, R is the gas constant, and T is the absolute temperature. Together with the following equation for μ_L

$$\mu_L = \mu_L^0 + RT\ln[\theta/(1-\theta)], \tag{5}$$

the final result is obtained as

$$\theta/(1-\theta) = (k_0 e^{2K\theta})\cdot C, \tag{6}$$

which is the same equation as that used by Levine *et al.*[2)] for the adsorption of methanol from an aqueous solution by a plain solid surface. Here,

$$k_0 = \exp[-(\mu_L^0-\mu_S^0)/RT], \tag{7}$$

and

$$K = \varepsilon/2RT. \tag{8}$$

The k_0 parameter is related to the strength of the adsorption from the solution to the adsorption monolayer, while K is related to the lateral interaction in the monolayer. The latter is so defined that $K<0$ for intermolecular repulsion, $K=0$ for the Langmuir

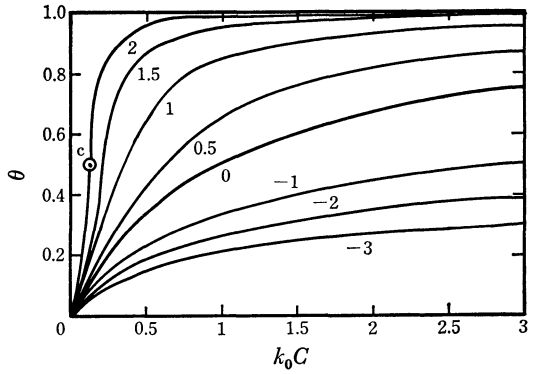

Fig. 1. Theoretical adsorption isotherms shown as the dependence of the fractional adsorption amount θ on k_0C, the parameter being K. The point C is the critical point where the phase separation in the adsorption monolayer starts.

case, and $K>0$ for intermolecular attraction. If $K>2$, phase separation occurs in the adsorption monolayer.[3] According to Eq. 6, the theoretical relations between θ and k_0C for various values of K are shown in Fig. 1. The C point, located at $\theta=0.5$, $k_0C=0.13534$ for $K=2$ in Fig. 1, shows the critical point at which the phase separation starts.

Equation of State of the Adsorption Monolayer. In the studies of the adsorption at the interface of a solution, the quantity measured experimentally is the surface tension, γ, of the solution, while the surface pressure, F, of the adsorption monolayer is defined by

$$F = \gamma_0 - \gamma, \tag{9}$$

where γ_0 is the surface tension of the solvent.

Theoretical equations for F can be derived by integrating the Gibbs equation:

$$F = \Gamma_0 RT\int_0^{\theta}\theta\left(\frac{\mathrm{d}\ln C}{\mathrm{d}\theta}\right)\mathrm{d}\theta. \tag{10}$$

By introducing Eq. 6 into Eq. 10,

$$(A_0/k_BT)F = -\ln(1-\theta) - K\theta^2 \tag{11}$$

is obtained, because $\Gamma_0 RT=k_BT/A_0$, where k_B is the Boltzmann constant. In the case of $K=0$, Eq. 11 is reduced, by using Eq. 6, to the Szyszkowski equation:

$$(A_0/k_BT)F = \ln(1+k_0C). \tag{12}$$

The equation of the state of the adsorption monolayer is derived from Eq. 11 by using Eq. 3:

$$(A_0/k_BT)F = \ln\left(\frac{A}{A-A_0}\right) - K\left(\frac{A_0}{A}\right)^2. \tag{13}$$

According to this equation, theoretical curves for various values of K are drawn in Fig. 2, where the relation between two dimensionless quatities, $(A_0/k_BT)F$ and (A/A_0) is shown instead of the F-A relation which is usually studied experimentally. It may be seen from Fig. 2 how a monolayer is expanded by the intermolecular repulsion ($K<0$) and is contracted by the intermolecular attraction ($K>0$).

The contraction of a monolayer by two-dimensional condensation is often examined by drawing the FA-A relation. Figure 3 shows the corresponding relation between the dimensionless quantities, FA/k_BT and $(A_0/k_BT)F$. Each theoretical curve has a minimum

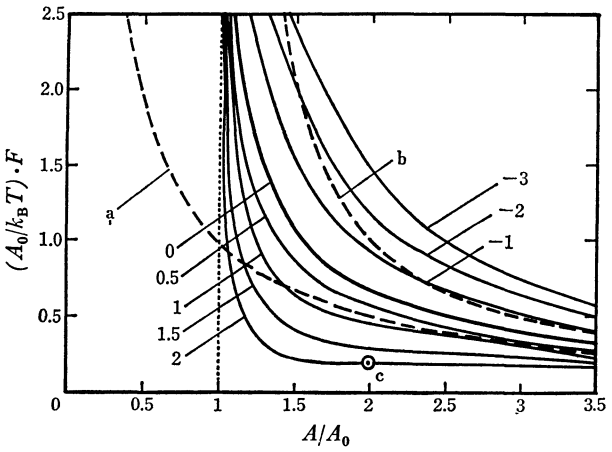

Fig. 2. Theoretical pressure-area curves of adsorption monolayers with various K values as indicated. The broken curve a is for $FA=k_BT$ and b for $F(A-A_0)=k_BT$.

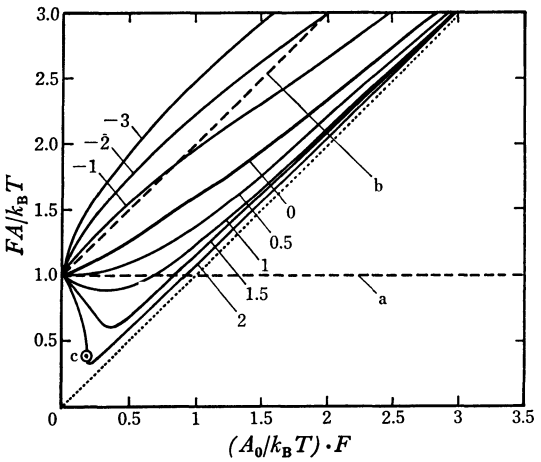

Fig. 3. Theoretical FA-A curves for various K values as indicated. The dotted line is for $A=A_0$. The broken straight line a is for $FA=k_BT$ and b for $F(A-A_0)=k_BT$.

point if $K>0.5$ and approaches to the asymptote, $A=A_0$, when F increases. If $K>2$, the entire curve is very close to the asymptote in the region where F is higher than that for the critical point, c, of the phase separation.

It may be emphasized here that the F-A relation, and also, therefore, the FA-A relation, of the adsorption monolayer are independent of the strength of the adsorption, because the equation of state, Eq. 13, does not contain the k_0 parameter. This conclusion is important both theoretically and experimentally. This means theoretically that there is no substantial difference between the adsorption monolayer and the insoluble monolayer. Experimentally, it is expected that the F-A relation or FA-A relation must be adequate for examining the intermolecular interaction in an adsorption monolayer, because the value of the K parameter may be determined on the basis of Fig. 2 or Fig. 3 without bothering to estimate the k_0 value. This expectation, however, was not realized because of the ambiguity brought in when the experimental γ-ln$C$ curve was differentiated graphically in order to obtain the value of Γ or A according to the Gibbs adsorption equation.

Therefore, a direct comparison between the experimental and theoretical γ-C relations is desirable in order to estimate the value of the K parameter.

Relation between the Surface Pressure and Concentration. The surface tension, γ, or the surface pressure, F, is given explicitly as a function of the concentration, C, if $K=0$, as has been shown in Eq. 12. If, however, $K\neq 0$, an explicit expression cannot be obtained; instead, the numerical relations between F and C for various values of K must be calculated by using Eqs. 6 and 11 simultaneously. This means that the following simultaneous equations must be solved numerically, taking θ as the parameter:

$$\left.\begin{aligned}(A_0/k_BT)F &= -2.303\log(1-\theta) - K\theta^2\\ \log(k_0C) &= \log\theta - \log(1-\theta) - 0.8686K\theta\end{aligned}\right\}. \quad (14)$$

The results are shown in Fig. 4, where dimensionless quantities, $(A_0/k_BT)F$ and k_0C, are used in place of F and C respectively.

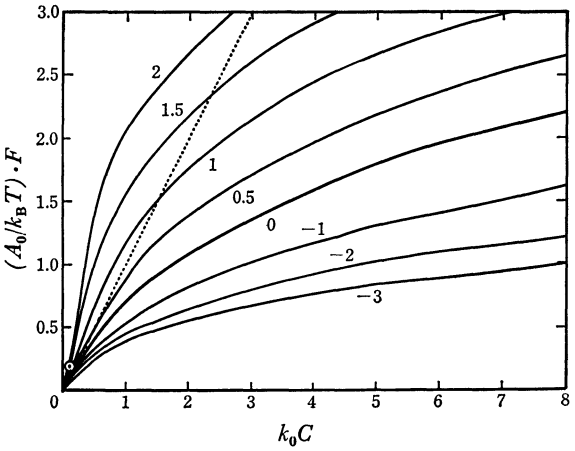

Fig. 4. Theoretical relations between the surface pressure F and concentration C, for various K values as indicated. The dotted line is the initial slope.

It might seem strange at first glance that the value of F, or the decrease of γ, is larger when the lateral intermolecular attraction is larger and when the value of K is larger for any given k_0 and (A_0/k_BT). This, however, does not mean that the adsorption monolayer of the larger lateral attraction shows a larger surface pressure at a given amount of adsorption; it does mean that the amount of adsorption is larger when the lateral attraction in the monolayer is larger, as has already been shown in Fig. 1.

To estimate the parameter values experimentally, two methods are commonly used, one in low-concentration, and the other in high-concentration, regions.

In the low concentration region ($\theta\rightarrow 0$), the expansion of $(A_0/k_BT)F$ in a power series of k_0C is performed by using the simultaneous equations 14; the following result is thus obtained:

$$(A_0/k_BT)F = k_0C + \left(K-\frac{1}{2}\right)(k_0C)^2 + \cdots. \quad (15)$$

According to this equation, it may be said that F is proportional to C if $k_0C\ll 1$ and that the proportionality coefficient is equal to $(k_0/A_0)k_BT$. This proportionality is considered to be helpful for the experimental determination of the parameter values. However, the theoretical curves in the low-concentration range, as shown in Fig. 5, start curving at an unexpectedly low concentration, except in the particular case of $K=0.5$, where the F-C relation is linear up to fairly large values of C because the coefficient of the C^2 term in Eq. 15 is zero. It may be seen from Fig. 5 that the concentration range where the F-C relation is not affected by the value of K and where the proportionality between F and C holds is as low as $(A_0/k_3T)F<0.03$. This means that the proportionality coefficient must be determined in the region where $F<0.4\times 10^{-3}$ N m^{-1} if $A_0=30\times 10^{-2}$ nm^2·molecule^{-1} at 25 °C. Experimentally, this is not always easy.

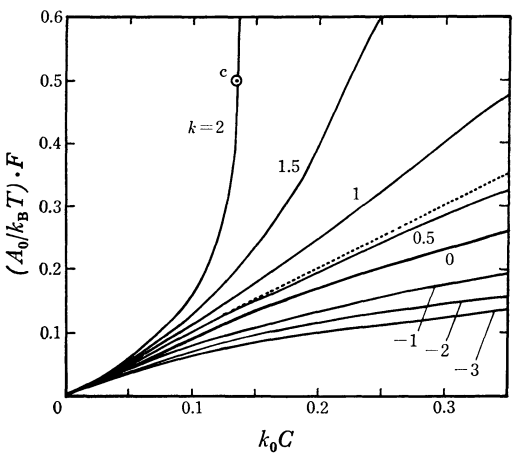

Fig. 5. Theoretical relations between F and C at a low concentration range. The dotted line is the initial slope, which is common to all curves and corresponds to the equation $F=(k_0/A_0)\,k_BTC$.

In the high-concentration region ($\theta\rightarrow 1$), the F-log C curve approaches an asymptotic straight line. The equation of this asymptote is obtained from Eq. 14:

$$(A_0/k_BT)F_{asymp} = K + \ln(k_0C) \quad (\theta\rightarrow 1). \quad (16)$$

Some of the theoretical curves obtained from Eq. 14 are shown in Fig. 6, together with the asymptotes of Eq. 16. It can be understood from Eq. 16 that the inclination of the asymptote of an F-log$C$ curve is equal to $(2.303\,k_BT/A_0)$, but it is clear from Fig. 6 that A_0 values thus estimated are acceptable only when K has a large positive value. If, for example, $K=0$, it may be seen from Fig. 6 that a correct value of the inclination may be obtained by using only the experimental data for $(A_0/k_BT)F>3.0$; this means that $F>41\times 10^{-3}$ N m^{-1} if $A_0=30\times 10^{-2}$ nm^2 molecule^{-1} at 25 °C. This condition is, however, not easy to realize experimentally, and it is impossible to fulfill when the monolayer collapses at this high surface pressure or when the concentration of the solution cannot be high enough because the solubility of the solute is not high enough. The method is, therefore, not applicable except for long-chain derivatives such as surfactants in which the K value may be supposed to be large.

As the conclusion of these considerations, it may be said that a method is needed which makes the estimation of the A_0, k_0, and K parameters possible by using the experimental data obtained in the intermediate

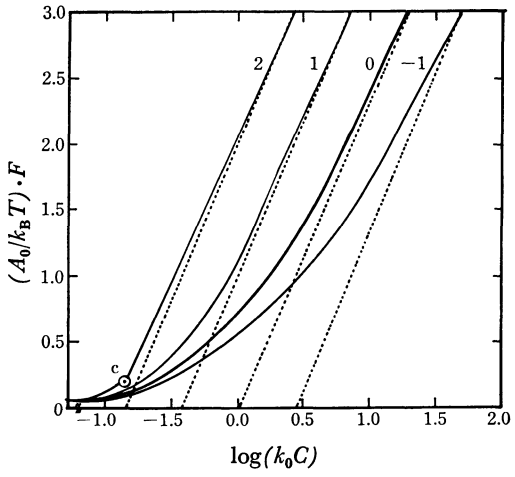

Fig. 6. Theoretical relations between F and log C for various K values as indicated. The dotted lines are the asymptotes.

concentration range.

Proposed Method to Determine Parameter Values. It has been found, after several trials, that the use of the relation between log (F/k_BTC) and log C is the most convenient for determining the values of A_0, k_0, and K. The theoretical curves of log $(F/k_BTC)+\log(A_0/k_0)$ against log $C+\log k_0$ are calculated by using Eq. 14 and are shown in Fig. 7 for the K values from 0 to 2 at regular intervals of 0.2. For $K>0.5$, each curve has a maximum point which corresponds to the θ_{max} given by the following equation:

$$\theta_{max} + \ln(1-\theta_{max}) + K\theta_{max}^2 = 0. \quad (17)$$

On the other hand, the experimental data are plotted, taking log (F/k_BTC) and log C on the ordinate and abscissa respectively, on the same scales as those of the theoretical plot in Fig. 7 and are superimposed on the latter so that the experimental data fit one of the theoretical curves. The shape of the theoretical curve for the best fit will give the K-value. Then, the k_0-value is obtained from the value of log C for log $C+\log k_0=0$, and the A_0-value, from the value of log (F/k_BTC) for log $(F/k_BTC)+\log(A_0/k_0)=0$.

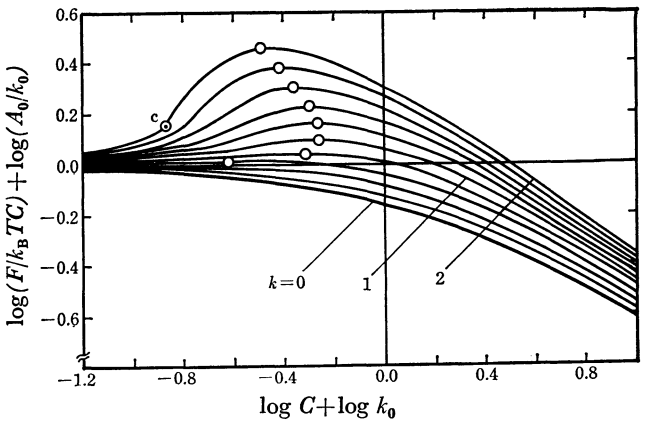

Fig. 7. Theoretical log (F/k_BTC)-log C curves for $K=$ 0(0.2)2. Open circles show the maximum points. The point c is the critical point of phase separation.

Comparison with Experimental Data

Parameter Values of Normal Alcohols. The experimental values of Posner *et al.*[4] were used to test the method proposed above. For example, the case of 25 °C is shown in Fig. 8, where the circles are experimental and the curves are theoretical. The parameter values thus obtained are given in Table 1, together with those obtained for other temperature values.

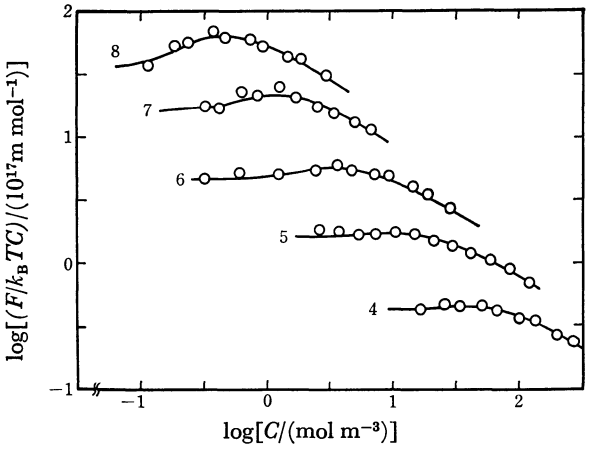

Fig. 8. Comparison between experimental values[4] (open circles) and theoretical curves for normal alcohols, which have the carbon numbers n as indicated, at 25 °C.

TABLE 1. PARAMETER VALUES OF NORMAL ALCOHOLS

Alcohol	Temp (°C)	K	$k_0\times10^3$ ($m^3\,mol^{-1}$)	$A_0\times10^2$ ($nm^2\cdot molecule^{-1}$)
Butyl	12	0.75	20.9	35.5
	25	0.75	14.8	34.7
	39	0.75	12.6	30.2
Pentyl	25	0.75	49.0	30.9
	39	0.75	37.2	30.9
Hexyl	12	1.00	251	38.9
	25	1.00	138	30.9
	39	1.00	123	33.9
Heptyl	12	1.25	525	30.9
	25	1.1	468	30.2
	39	1.1	302	29.5
Octyl	12	1.5	1700	33.1
	25	1.5	1000	29.5
	39	1.4	708	26.9

The k_0 parameter is essentially the equilibrium constant between solute molecules adsorbed on the surface and dissolved in the solution, and it is related to the change in the standard chemical potential due to the adsorption according to Eq. 7. Before the standard affinity of adsorption $(-\Delta\mu^0)$ is calculated, however, the experimental parameter value, k_0, in $m^3\,mol^{-1}$ based on the molar concentration, C, must be recalculated to the dimensionless "unitary" quantity,[5] k_x, based on the mole fraction, x,

$$k_x = (C/x)k_0 \simeq (d_1/M_1)k_0$$
$$= 55.34(k_0\times10^3)/(m^3\,mol^{-1}), \quad (18)$$

for aqueous solutions at 25 °C, where d_1 and M_1 are

Table 2. Affinity of the adsorption and energy of lateral interaction

Alcohol	Temp (°C)	$-\Delta\mu^0$ (kcal mol^{-1})		ε (kcal mol^{-1})	
Butyl	12	4.00	(4.02)	0.85	(0.89)
	25	3.98		0.89	
	39	4.07		0.93	
Pentyl	25	4.69	(4.72)	0.89	(0.91)
	39	4.74		0.93	
Hexyl	12	5.41	(5.40)	1.13	(1.19)
	25	5.30		1.19	
	39	5.48		1.24	
Heptyl	12	5.83	(5.97)	1.42	(1.36)
	25	6.03		1.30	
	39	6.04		1.37	
Octyl	12	6.49	(6.51)	1.70	(1.74)
	25	6.48		1.78	
	39	6.57		1.74	

( ): Averages.

the density and the molecular weight of water respectively.

The values of the standard affinity of adsorption obtained by the following equation from the k_0-values of Table 1 are shown in Table 2 (1 cal=4.184 J):

$$-\Delta\mu^0 = RT \ln k_x. \tag{19}$$

From these tables it may be seen that $(-\Delta\mu^0)$ does not depend much on the temperature, although k_0 and, therefore, k_x decrease with increase in the temperature. The energy of lateral interaction, ε, calculated by Eq. 8 from the K values given in Table 1 is shown in Table 2 as well. Since the temperature dependences of $-\Delta\mu^0$ and ε are not large, the average values (shown in parentheses in Table 2) are plotted against the number of carbon atoms of alcohols, n, in Fig. 9. It may be seen that the value of ε is about 1/4 of $-\Delta\mu^0$ for each alcohol in this region of n.

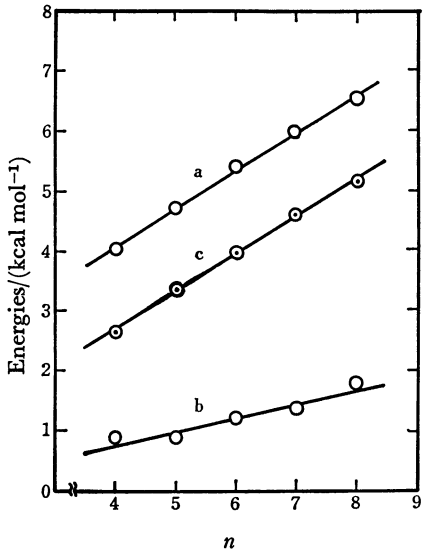

Fig. 9. Dependence, on the carbon number n, of (a) the standard affinity $-\Delta\mu^0$ of Eq. 19, (b) the energy of lateral interaction ε of Eq. 8 and (c) the standard free energy of adsorption $-\Delta G^0$ of Eq. 25.

The relations of $-\Delta\mu^0$ and of ε against n in Fig. 9 are linear and give the following empirical equations:

$$-\Delta\mu^0/(\text{kcal mol}^{-1}) = 1.60 + 0.62n \tag{20}$$

and

$$\varepsilon/(\text{kcal mol}^{-1}) = -0.16 + 0.23n. \tag{21}$$

Equation 20 means that the affinity of adsorption is 620 cal mol^{-1} per methylene group and 1600 cal mol^{-1} per hydroxyl group. The latter value, however, depends on the selection of the standard states. The former value, 620 cal mol^{-1}, is not much different from Traube's value,[6] 650 cal mol^{-1}. The former value obtained for n=4—8 is, however, a little smaller than the value, 682 cal mol^{-1}, for n=12—16 obtained for disodium monoalkyl phosphates,[7] probably because of the difference in the range of n. Equation 21 means that the energy of lateral attraction per methylene group is 230 cal mol^{-1}, while the energy of lateral repulsion per hydroxyl group is 160 cal mol^{-1}.

On the other hand, Ward and Tordai[8] and also Posner *et al.*[4] calculated the standard free energy of adsorption by means of

$$\Delta G^0 = -RT \ln (\alpha/k_B T\delta), \tag{22}$$

where δ is the thickness of the adsorption monolayer and α is the Traube constant defined at an infinite dilution by:

$$\alpha = \lim_{C\to 0} (F/CN_A), \tag{23}$$

where N_A is the Avogadro number.

According to our Eq. 15,

$$\alpha = k_B T(k_0/A_0 N_A), \tag{24}$$

therefore, we have

$$-\Delta G^0 = RT \ln (k_0/A_0\delta N_A). \tag{25}$$

As for the parameter values to be used in this equation, the values of k_0 and A_0 have been shown in Table 1; the values of δ given by Posner *et al.*[4] are cited in Table 3. The values of $-\Delta G^0$ thus calculated are given in the same table, together with the values reported by Posner *et al.*,[4] the latter being indicated by $-\Delta G_p{}^0$. It may be seen that these values are in good agreement with each other. This is because, at an infinite dilution,

Table 3. Standard free energy of adsorption as calculated by means of Eq. 25

Alcohol	$\delta\times 10$ (nm)[4]	Temp (°C)	$-\Delta G^\circ$ (kcal mol^{-1})		$-\Delta G_p{}^\circ$ (kcal mol^{-1})[4]
Butyl	8.8_9	12	2.26	(2.65)	2.66
		25	2.59		
		39	2.70		
Pentyl	9.5_3	25	3.32	(3.32)	3.36
		39	3.31		
Hexyl	9.9_2	12	3.96	(3.95)	4.05
		25	3.92		
		39	3.97		
Heptyl	10.1_2	12	4.49	(4.58)	4.72
		25	4.64		
		39	4.60		
Octyl	10.2_4	12	5.11	(5.13)	5.42
		25	5.10		
		39	5.18		

( ): Averages.

the lateral interaction between the adsorbed molecules becomes negligible and the $k_0\exp(2K\theta)$ term in Eq. 6 approaches k_0.

Since the temperature dependence of $-\Delta G^0$ is negligible, the average values are plotted in Fig. 9. The linear relation in the figure gives the empirical relation

$$-\Delta G^0 = 0.17 + 0.63n. \quad (26)$$

The free energy of adsorption per methylene group is, therefore, 630 cal mol^{-1}, which is almost the same as the value of Eq. 20. This can be understood directly from Fig. 9 in view of the fact that the straight lines for $-\Delta\mu^0$ and $-\Delta G^0$ are parallel with each other.

By comparing Eqs. 19 and 25, it can be understood that the parallel relation means that the molar volume of the adsorption monolyer, $V_m = A_0\delta N_A$, obtainable from our value of the molecular area, A_0, is independent of the number of carbon atoms, n, of the alcohols. The value of V_m at 25 °C is actually almost constant and is 181.7×10^{-6} m^3 mol^{-1} on the average from butyl to octyl alcohols, while the molar volume of the liquid, V_l, increases from 91.6×10^{-6} m^3 mol^{-1} in butyl alcohol to 157.8×10^{-6} m^3 mol^{-1} in octyl alcohol, according to the increase in the molecular weight, because the density does not increase so much. This seems to be an interesting point.

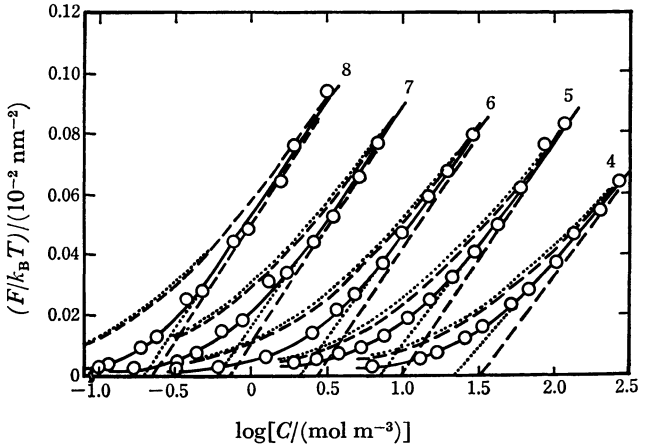

Fig. 10. Comparison between experimental values (open circles)[4] and theoretical solid curves drawn by Eq. 14 at 25 °C for normal alcohols whose carbon numbers are as indicated. Broken straight lines are calculated by Eq. 16, and broken curves are the Szyszkowski curves corresponding to them. Dotted straight lines are empirical and dotted curves are the corresponding Szyszkowski's.

Relation between F *and log* C. It is shown in Fig. 10 that the agreement is good between the experimental data by Posner *et al.*[4] at 25 °C (open circles) and the theoretical curves (solid lines) drawn according to Eq. 14 by using the parameter values given in Table 1. In Fig. 10 the asymptotes, too, are shown by broken straight lines according to Eq. 16, using the same parameter values.

Table 4. Comparison of parameter values of Eq. 27 at 25 °C

Alcohol	$A_0'\times10^2$ (nm^2·molecule^{-1})	$k_0'\times10^3$ (m^3 mol^{-1})	A_0'/A_0	$k_0'/(k_0e^K)$
Butyl	39.6	44.7	1.14	1.43
Pentyl	34.6	142	1.12	1.37
Hexyl	34.1	490	1.10	1.31
Heptyl	32.2	1700	1.07	1.21
Octyl	31.1	5130	1.05	1.14

Experimentally, however, one might draw asymptotes like those shown by dotted straight lines in Fig. 10. For these asymptotes, if one used the following equation,

$$A_0'F_{asymp}/k_BT = \ln k_0' + \ln C \quad (27)$$

which can be derived from Szyszkowski's Eq. 12, the parameter values, A_0' and k_0', given in Table 4 may be obtained. By using these values for A_0 and k_0 of Eq. 12, Szyszkowski's theoretical curves are drawn in Fig. 10 by dotted curves; those curves are not, however, in agreement with the experimental values.

This discrepancy is partly due to the overestimation of the parameter values shown in Table 4 in that A_0'/A_0 and $k_0'/(k_0e^K)$ are larger than 1.0. Here, k_0' is compared to k_0e^K, because the latter is the value obtained from the broken straight lines, as can be understood by comparing Eq. 27 with Eq. 16. Even if the values of A_0 and k_0e^K are inserted into A_0 and k_0 of Eq. 12, however, the Szyszkowski curves shown by broken curves in Fig. 10 are still distant from the experimental values. The discrepancy is, therefore, mainly the result of the use of the Szyszkowski equation. It can be concluded that the use of Eq. 14, which takes the lateral interaction between the adsorbed molecules into account, is indispensable in explaining the experimental results over the entire concentration range.

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