Behavior of Surface Active Molecules at Interface. I. Statistical Mechanical Studies on Head Contact and Chain Contact

By Masayuki NAKAGAKI and Saiichi IIDA

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The pressure-area curves of condensed monomolecular films are, in general classified in two types shown in Fig. 1. The one is curve a, which stands up with a steep slope at the area A_1, e.g. condensed film of saturated fatty acid on distilled water. The other is curve b, where the pressure bigins to increase gradually at the area A_2, and coincides with curve at G, e.g. the condensed film of saturated fatty acid on dilute HCl solution (N/10∼N/100).

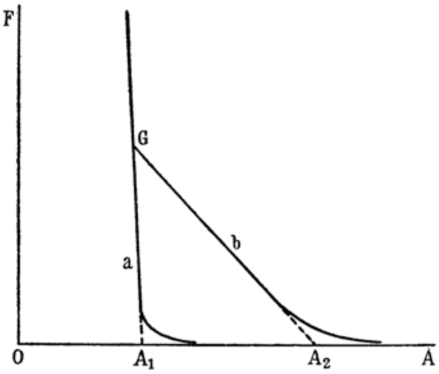

Fig. 1. Schematic diagram of pressure-area curve of condensed films.

For saturated hydrocarbon chain, the value of A_1 is 20.5 Å², which depends upon neither length of the chain nor the sort of end group. On the other hand, the value of A_2 depends upon the sort of end group. According to these empirical facts, Adam[1] proposed the idea of head contact and chain contact. The state of A_1 is considered to be a closs-packed chain, and 20.5 Å² is assumed to be the cross sectional area of the hydrocarbon chain. While, the state of A_2 is thought to be a close-packed head, and the value of A_2 is equal to the cross sectional area of end group. When the film with close-packed head is further compressed, some of the end groups are dipped into water, and the film at last reaches the state of close-packed chain at G.

Statistical Mechanical Treatment

The idea of head contact and chain contact is formulated using a model as follows. When a film with close-packed head (A_2) is compressed gradually, some of the end groups are dipped into water. Let the fraction of of dipped end group be x, and the energy required to dip one end group be w. It is assumed that the cross sectional area of hydrocarbon chain chain is A_H and that of the end group is A_P; then the average area occupied by one molecule, A_b, is

$$\left.\begin{aligned} & A_b = xA_H + (1-x)A_P = A_P - xB \\ \text{where} \quad & B = A_P - A_H \end{aligned}\right\} \tag{1}$$

Therefore, the free area per one molecule, A_f, is

$$A_f = A - A_b = A - A_P + xB \tag{2}$$

where A is the total area per one molecule.

Considering that the state of molecules in condensed film is analogous to that in a two-dimensional liquid, partition function Z may be formulated. The Gibbs free energy, G, is then calculated by

$$G = -kT \ln Z \tag{3}$$

since the Gibbs free energy is approximately equal to the Helmholtz free energy for condensed systems. As the result,

$$\begin{aligned} G/nkT = & -\ln (2\pi mkT/h^2) + (\phi/kT) + (xw/kT) \\ & -\ln A_f + \{x \ln x + (1-x) \ln (1-x)\} \end{aligned} \tag{4}$$

is obtained, where n is the number of molecules in the film, ϕ is the potential energy of a molecule on the surface referring the energy of molecules in gaseous film (zero), so that ϕ is the negative of the energy of condensation in monomolecular film, ($\phi < 0$), and w is the energy required to dip one end group into water as shown in Fig. 2 ($w > 0$).

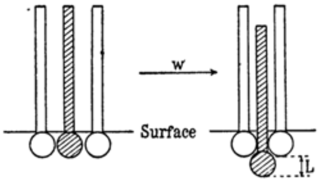

Fig. 2. Schematic explanation of energy w.

The last two terms of Eq. (4) correspond to the mixing entropy of molecules, whose polar groups are on and under the surface. The fraction of molecules dipped into water, x,

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[1] N.K. Adam, "Physics and Chemistry of Surfaces", Oxford (1938), p. 50.

is determined by the condition of minimum free energy:

$$(\partial G/\partial x)_{A,T}=0 \tag{5}$$

Then,

$$x/(1-x)=\{\exp.(-w/kT)\}\times\left\{\exp.\left(\frac{B}{A-A_P+xB}\right)\right\} \tag{6}$$

is obtained. From this equation, it is clear that x becomes greater when the energy required to dip molecule, w, is small, or temperature is higher or the film is compressed and A becomes smaller.

The surface pressure is obtained by

$$F=-(\partial G/\partial S)_{T,n}=-(1/n)(\partial G/\partial A)_{T,n} \tag{7}$$

where S is the area of film, that is

$$S=nA \tag{8}$$

Using Eqs. (4), (6) and (7) and assuming that w is independent to A,

$$F/kT=-(1/kT)(\partial \phi/\partial A)+(1/A_f) \tag{9}$$

is obtained. As for right side of Eq. (9), the first term shows the pressure to contract the film by the cohesional force and the second term shows the thermal pressures is equal to the surface pressure observed. The cohesional pressure and the thermal pressure are both very great compared to their difference, so it will be perhaps very difficult to calculate the absolute value of the surface pressure theoretically. The assumption will be, however, reasonable that the potential energy ϕ is a function of intermolecular distance only, and the value of $(\partial\phi/\partial A)$ is a function of A only. Then, it is possible to calculate the difference of the surface pressure of two states of the same value of A.

Imagine a state where molecules are always in chain contact. The surface pressure of this imaginary state is assumed as F_1, and the real surface pressure of a film of the same value of A is described as F. Then the difference of them is,

$$\frac{\varDelta F'}{kT}=\frac{F}{kT}-\frac{F_1}{kT}=\frac{1}{A_f}-\frac{1}{A-A_H} \tag{10}$$

since the free area of the imaginary state is $(A-A_H)$. Then, using (2) and (6),

$$\frac{B}{kT}\varDelta F'=(1-x)\left(\frac{w}{kT}+\ln\frac{x}{1-x}\right)^2\Big/\left\{1+(1-x)\left(\frac{w}{kT}+\ln\frac{x}{1-x}\right)\right\}$$

$$\frac{A-A_P}{B}=\left(\frac{1}{\dfrac{w}{kT}+\ln\dfrac{x}{1-x}}\right)-x \tag{11}$$

are obtained. Using these equations, the relation between $(\varDelta F'B/kT)$ and $(A-A_P)/B$ is calculated for a given set of x and (w/kT).

It should be stressed here that the state assumed above as a standard state, that is the state of all chain contacts, is different from the state of $w=0$. The words close-packed chain, named by Adam for curve a in Fig. 1, may suggest that the molecules in the film are always in chain contact, but such a state can never be realized. The most compact state realizable is a state of $w=0$. In the case of $w=0$, x approaches $\frac{1}{2}$ when the film is sufficiently widened, that is $A_f\rightarrow\infty$, (see Eq. (6)). This owes to the term of mixing entropy of dipped and not dipped molecules in Eq. (4). By a sufficient compression of the film, x approaches unity when A is nearly equal to A_H. Anyway, the state of $w=0$ is the most compact state realizable, so it should correspond to the curve a in Fig. 1, and the value of $\varDelta F'$ in Eqs. (10) and (11) for $w=0$ is shown as $\varDelta F_0'$. While the curve b in Fig. 1 corresponds to a state where w is not equal to zero. The difference

$$\varDelta F=\varDelta F'-\varDelta F_0' \tag{12}$$

may be calculated numerically from Eq. (11) as a function of A, for a given values of w, B and A_P. On the other hand, observed surface pressure of curve a and b in Fig. 1 are expressed as F_0 and F, respectively. Then, $\varDelta F$ is obtained experimentary by

$$\varDelta F=F-F_0 \tag{13}$$

and compared with the theoretical value of Eq. (12).

Comparison with Experiment

To facilitate the comparison, $\varDelta F$–A relation is recalculated and plotted as $\eta-\xi$ relation, where

$$\xi=\frac{A-A_P}{A_P-A_H}-\frac{A-A_P}{B} \tag{14}$$

$$\eta=\left(\frac{A_P-A_H}{kT}\right)\varDelta F=\frac{B}{kT}\varDelta F \tag{15}$$

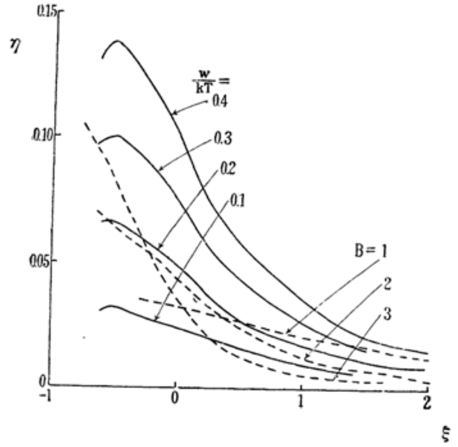
Then, from the theoretical stand point, $\eta-\xi$ relation is determined by a parameter (w/kT), since x may be eliminated, in principle, from two equations in Eq. (11) (see Fig. 3). While, using the experimental value of $\varDelta F$ and A, values of ξ and η varies with the values of B and A_P as shown in Eqs. (14) and (15). Assume that

$$A_H=20.6 \quad (\text{Å}^2) \tag{16}$$

then,

$$A_P=A_H+B=20.6+B \tag{17}$$

Therefore, an experimental ΔF–A relation is recalculated to a $\eta-\xi$ relation for a given value of a parameter B. The data of Adam[2] for saturated fatty acid, is shown in Fig. 3 for some values of B. From the figure, it is seen that (w/kT) is nearly equal to 0.2, and B is nearly equal to 2.



—— theor., - - - exper.
Fig. 3. η–ξ Selations.

To obtain more accurate values of B and w/kT, the variation of η for a given value of ξ is studied. For a given value of ξ, and for a certain value of B, an experimental value of η is determined, and to obtain the same value of η theoretically, a value of w/kT is determined. Therefore, for a given value of ξ, a (w/kT)-B relation is obtained as shown in Fig. 4. For one value of ξ, one curve is obtained, and they cross nearly at one point P. Values of w/kT and B, corresponding to the point P, are the most convenient values, that is

$$\left.\begin{aligned} w/kT &= 0.17_5 \\ B &= 1.7_5 \end{aligned}\right\} \qquad (18)$$

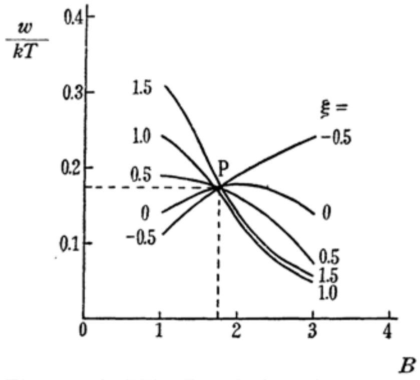


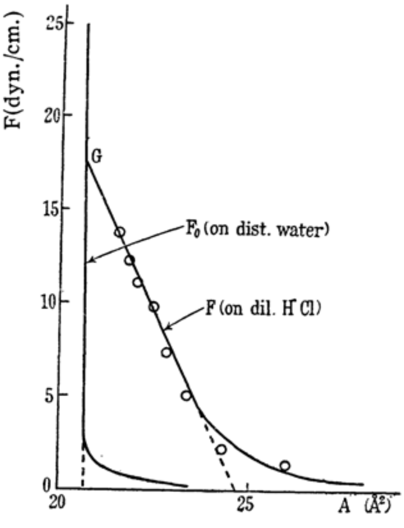
Fig. 4. $(w/kT)-\mathrm{B}$ relation for saturated fatty acid.

Using these values and experimental value of F_0, the value of F is calculated. The results in Fig. 5 showes a good agreement with experimental value of Adam.

The method of calculation described above is very complicated, though the results are satisfactory. The more simplified method is desirable. The experimental relation in Fig. 1 a is simplified as Fig. 6. The low pressure tail (hatched portion) is neglected, and the curve F_0 is assumed to be zero for $A > A_{\mathrm{H}}$, and it is assumed that the curve stands up vertically at $A = A_{\mathrm{H}}$. In Fig. 1 b the curve F is linear from A_2 to G, where the tail at lower pressure part (hatched in Fig. 6) is also neglected. The difference of A_{H} and A_2 is written as A_{S}, and the pressure at G as F_{S}. Then, at $\xi=0$, or at $A = A_{\mathrm{P}} = A_{\mathrm{H}} + B$

$$\left.\begin{aligned} \Delta F &= (A_{\mathrm{S}} - B)F_{\mathrm{S}}/A_{\mathrm{S}} \\ -(\mathrm{d}\Delta F/\mathrm{d}A) &= F_{\mathrm{S}}/A_{\mathrm{S}} \end{aligned}\right\} \qquad (19)$$

are obtained. On the other hand, the the-



—— obsd., ○ calcd.
Fig. 5. Observed and calculated values for saturated fatty acids.

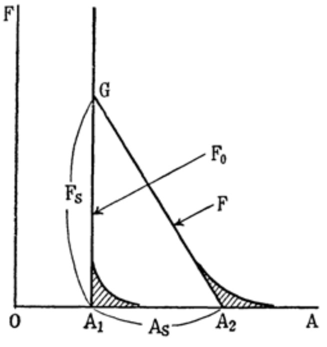


Fig. 6. Simplified F-A diagram.

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[2] N.K. Adam, *Proc. Roy. Soc.*, **A101**, 452 (1922).

oretical treatment is simplified as follows. From the theoretical curve in Fig. 3, the value of η and $(d\eta/d\xi)$ at $\xi=0$ are determined at a function of w/kT. Then it is seen that they are linear to w/kT, at least within the range of $w/kT=0\sim0.6$. This linear relation is, using Eqs. (14) and (15), at $A=A_H+B$,

$$\left.\begin{aligned}\frac{B}{kT}\Delta F&=0.250\frac{w}{kT}\\ -\frac{B^2}{kT}\frac{d\Delta F}{dA}&=0.190\frac{w}{kT}\end{aligned}\right\}\tag{20}$$

Using Eqs. (19) and (20)

$$B=A_P-A_H=0.432\,A_S\tag{21}$$

$$w/kT=0.982\ A_SF_S/kT\tag{22}$$

are obtained. Using these equations, the values of B and w/kT are calculated. As for the saturated fatty acid shown in Fig. 5, $F_S=17.5$ dyn./cm. $A_H=20.6$ Å^2, $A_2=24.7$ Å$_2$, and therefore $A_S=4.1$ Å^2. Then, at 25°C,

$$\left.\begin{aligned}B&=1.7_7\\ w/kT&=0.17_4\end{aligned}\right\}\tag{23}$$

are obtained from Eqs. (21) and (22). These are in good agreement with Eq. (18), obtained by a strict method.

To study more cases, data summarized by N.K. Adam[3] are used. Those and the results calculated from them using Eqs. (21) and (22) are cited in Table I, where it is assumed that $A_H=20.5$ Å^2. The value of F_S marked in Table I by * are obtained by an extrapolation, assuming that the F–A curve extends linearly to $A=20.5$ Å^2. The values of w obtained by this method are, in general, very small; that is, less than 0.5 kcal./mol. For a few molecules, w is greater than 1 kcal./mol. The value of w corresponds to the energy required to dip an end group into water. It is, however, not the energy of solution of the whole molecule, but it is, as shown in Fig. 2, the energy to make the distribution of end group disorder. It is the energy required to dip hydrocarbon chain by the length of end group, (L in Fig. 2), if the hydration of the end group does not change before and after the dipping. Therefore, molecules of longer end group should have greater w values. Then it is acceptable that the sequence of w values in Table I is:

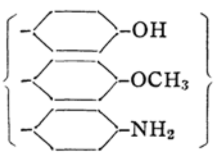
OH<COOH<NH·CO·CH$_3$<CH: CH·COOH<
-OH, etc. ≃ COOCH$_2$CHOHCH$_2$OH
<choresterol

Compared with this, w of nitril seems too large. Interaction between end groups should be, perhaps, taken into consideration. As for the value of the cross sectional area of the end group, A_P, Anam considered that A_2 is the cross section of end group, but by Eq. (21), A_P is somewhat smaller than A_2, and the difference to A_H is not so great as that by Adrm. This is rather in agreement with molecular models. Therefore, the state at A_2 is not the close-packed head, but it is a state of looser packing.

Mixed Monolayers

Harkins and Florence[4] measured the presure-area relations for stearic acid, stearyl alcohol, and 1:1 mixture of them. The values of A_H of these three cases differ from each other, but they are 20.0∼20.5 Å$_2$. For simplicity, it is assumed that A_H is 20.0 Å^2, and linear relation is extrapolated to $A=$

TABLE I
CALCULATED VALUE OF A_P w
(A_H is assumed to be 20.5 A^2)

Substances	End groups	A_2 (Å^2)	A_S (Å^2)	F_S (dyn./cm.)	B (Å^2)	A_P (Å^2)	w/kT	w (Kcal./mol.)
Alcohols	–CH$_2$OH	21.6	1.1	6.7	0.48	21.0	0.018	0.01
Acids	–COOH	25.1	4.6	17.3	2.0	22.5	0.193	0.12
Acetamides	–NH·CO·CH$_3$	24.2	3.7	25.	1.9	22.1	0.225	0.14
Isooleic acid	–CH: CH·COOH	28.7	8.2	15.2	3.5	24.0	0.303	0.18
α-Monoglycerides	–COOCH$_2$·CHOH·CH$_2$OH	26.3	5.8	45.3*	2.5	23.0	0.639	0.38
Nitrils	–C≡N	27.7	7.2	37.5*	3.1	23.6	0.657	0.39
p-Substituted benzene	 -OH -OCH$_3$ -NH$_2$	24.0	3.5	79.5*	1.5	22.0	0.677	0.41
Choresterterol	——	40.8	20.3	847. *	8.8	29.3	4.18	2.5

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[3] N.K. Adam, "Physics and Chemistry of Surfaces", Oxford (1938), p. 49.

[4] W.D. Harkins and R·T. Florence, *J. Chem. Phys.*, 6, 847 (1938).

20.0 A^2 to obtain the value of F_S. Calculated values of A_P and w from these data by Eqs. (21) and (22) are cited in Table II, compared with that of Adam in Table I.

TABLE II
CONDENSED FILM OF FATTY ACID, ALCOHOL AND MIXTURE OF THEM

	Film	Adam	Harkins & Florence	Nakagaki & Iida
A_P (Å^2)	RCOOH	22.5	21.8	22.4
	RCOOH +R′OH	—	21.3	21.9
	R′OH	21.0	20.8	31.2
w (kcal./mol.)	RCOOH	0.12	0.15	0.18
	RCOOH +R′OH	—	0.09	0.14
	R′OH	0.02	0.04	0.09

The present autors obtained the pressure-area curves for stearic acid, cetyl alcohol and 1:1 mixed film of them. Stearic acid (m.p. 71.1°C) and cetyl alcohol (m.p. 50.2°C) used are those provided by Nippon Yushi KK. A Wilhelmy type tensiometer with torsion balance is used with grass trough and glass barrier, paraffin with Merck's paraffine (m.p. 46~48°C). The substrate was N/1000 HCl solution. Point G in Fig. 1 is observed at about $A=20$ Å^2, so that the data were treated just as those of Harkins and Florence. The results obtained are also cited in Table II. It is seen that A_P and w of 1:1 mixed monolayer are cloth to the average of both components.

Summary

The idea of head contact and chain contact proposed by Adam was formulated by statistical mechanics, introducing the energy required to dip one end group into water, w. It is concluded that the value of w is less than 1 kcal./mol. for most of molecules examined, and it is greater when the length of the group is longer. The cross sectional area of the end group, A_P, is concluded to be smaller than that estimated by Adam. As for a mixed monolayer, the value of w and A_P were almost equal to the average of components.

Faculty of Living Science,
Osaka City University,
Osaka