*Behavior of Surface Active Molecules at an Interface. II. Statistical Thermodynamics of Monolayers of Rod-Like Molecules**

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(Received May 20, 1959)

A monolayer is often considered to be a two-dimensional system. However, this standpoint is not acceptable in detailed discussions, because a monolayer has a certain thickness and has a thermodynamic freedom in the direction perpendicular to the monolayer as well as in the two directions along the interface. An effort to consider the monolayer as a three-dimensional existence has been made in the preceding paper of this series[1] by considering the possibility that the end groups of the molecules in a monolayer are not necessarily on one plane, in order to explain the shape of the pressure-area curves of condensed monolayers.

Another example that definitely requires the three-dimensional consideration comes out from rather expanded monolayers in which molecules are supposed to be inclined to the normal of the interface so that the collision diameter of the molecules in the monolayer depends on the degree of the inclination of the molecules. This will be discussed in the present paper.

As for the equation of the state of the monolayer insoluble in the substrate, it has already been pointed out by Akamatsu and the present author[2] that the two dimensional analogue of the van der Waals equation can be used. Then, the equation applicable, at least empirically, is:

$$(F+a/A^2)(A-A_0)=kT \qquad (1)$$

where F is the surface pressure, A is the area per one molecule, k is the Boltzmann constant, T is the absolute temperature and a and A_0 are constants. A_0 corresponding to the constant b in the van der Waals equation is given by

$$A_0=(\pi/2)d^2 \qquad (2)$$

if the molecules are spherical and the diameter is d. However, fatty acid molecules and substances of much interest in surface chemistry is not spherical but is rod-like. If all the rod-like molecules are vertical to the interface and thickness of each molecule is d in diameter, it is then obvious that Eq. 2 can be used. Generally the rod-like molecules are, however, inclined to the interface or lying flat on the interface, so that Eq. 2 can not be used. For the molecules inclined to the interface, theoretical equations to be used instead of Eq. 2 will be derived, and the equations will be applied to experimental data already known in literature.

Theoretical Calculation of the Constant A_0

Principle of the Calculation. — For three-dimensional solutions, Zimm[3] calculated the van der Waals constant b for rod-like

* Presented before the 11th Symposium on Colloid Chemistry, the Chemical Soeiety of Japan, Sendai, Sept. 5, 1958.

1) M. Nakagaki, This Bulletin, **29**, 64 (1956).

2) H. Akamatsu and M. Nakagaki, ibid., **23**, 232 (1950).

3) B. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

molecules by using the method of McMillan and Mayer[4]. This method is to obtain the second virial coefficient from the value of the phase integral over the entire range of the overlapping of two molecules. By analogy with the three-dimensional osmotic pressure equation in the above mentioned papers, the second virial coefficient A_2 in the expression of the surface pressure F as a power series of surface concentration c:

$$F=\boldsymbol{R}T\{(1/M)c+A_2c^2+\cdots\cdots\} \quad (3)$$

is given by the equation,

$$A_2=-(\boldsymbol{N}_0/2SM^2)\int g_2\{2\}\,\mathrm{d}\,\{2\} \quad (4)$$

where $\boldsymbol{N}_0$ is the Avogadro number, M is the molecular weight of the surface active substance, S is the area of the interface. The integral will be explained later on. Since the surface concentration c is related to the area per one molecule A by the equation:

$$c = M/\boldsymbol{N}_0A \quad (5)$$

Eq. 3 is rewritten as

$$FA/\boldsymbol{k}T=1+(A_2M^2/\boldsymbol{N}_0)(1/A)+\cdots\cdots \quad (6)$$

On the other hand, Eq. 1 expanded in a power series of $(1/A)$ is

$$FA/\boldsymbol{k}T=1+(A_0-a/\boldsymbol{k}T)(1/A)+\cdots\cdots \quad (7)$$

where the term A_0 comes from the repulsion due to the overlapping of two molecules and the term $(a/\boldsymbol{k}T)$ comes from the intermolecular attraction.

On comparing Eqs. 6 and 7, two methods will be suggested for further calculations. The one, which is theoretically accurate but difficult to put in practice, is to calculate the integral in Eq. 4 by taking both the overlapping and the attraction into account, and to assign the value of $(A_2M^2/\boldsymbol{N}_0)$ thus obtained to $(A_0-a/\boldsymbol{k}T)$. The other method, which is theoretically rather arbitrary but easy to put in practice, is to calculate the integral in Eq. 4 by taking only the overlapping into account and neglecting the intermolecular attraction, and to assign the value of $(A_2M^2/\boldsymbol{N}_0)$ thus obtained to A_0. The latter method is adopted in the present paper because the term A_0 is of main interest and because the calculation of the integral is very complicated if the first method is used. Therefore,

$$A_0=-(1/2S)\int g_2\{2\}\,\mathrm{d}\,\{2\} \quad (8)$$

4) McMillan and Mayer, *J. Chem. Phys.*, **13**, 376 (1954).

The g-function of two molecules g_2 is calculated from distribution functions F_n by the equation

$$g_2(1,2)=F_2(1,2)-F_1(1)F_1(2) \quad (9)$$

where the suffix of both g- and F-functions designates the number of molecules in the system considered, and $\{n\}$ means the assembly of all the coordinates of n molecules, while (i) means the coordinates of the i-th molecule. The distribution function $F_2(1,2)$ must be zero in the region where the two molecules overlap. On the other hand, in the region where the molecules do not overlap, the function must be a constant, since the intermolecular attraction is to be neglected in the present method of the calculation. The value of the constant is determined by a normalization equation,

$$(1/S^n)\int F_n\{n\}\,\mathrm{d}\,\{n\}=1 \quad (10)$$

This equation can be rewritten as

$$F_n\{n\}=S^n/\int \mathrm{d}\,\{n\} \quad (11)$$

if $F_n\{n\}$ is a constant.

The Case in which All Molecules are Vertical to the Interface ($\theta=0°$).—Since all the rod-like molecules are assumed to be vertical to the interface, the overlapping of two circles of diameter d in one plane is to be considered. Therefore, the result must be identical with the case of spherical molecules given by Eq. 2. The calculation will be described in some detail for this simplest case in order to explain the process followed repeatedly in the later part of this paper.

As shown in Fig. 1a, the location of the axis of rod 1 is given by the coordinates X and Y, and that of rod 2 relative to rod 1 is given by the coordinates r and φ. Then,

$$\mathrm{d}\{2\}=\mathrm{d}X\mathrm{d}Y r\mathrm{d}r\mathrm{d}\varphi \quad (12)$$

By using Eq. 11,

$$F_2(1,2)=\begin{cases}1 & \text{when rods 1 and 2 do not overlap}\\ 0 & \text{when rods 1 and 2 overlap}\end{cases} \quad (13)$$

$$F_1(1)=F_1(2)=1$$

Now, rods 1 and 2 overlap when $0<r<d$, so that by Eq. 9,

$$\begin{aligned} g_2(1,2)&=-1 \quad \text{when } 0<r<d\\ g_2(1,2)&=0 \quad \text{in all other ranges of coordinates}\end{aligned} \quad (14)$$

Therefore,

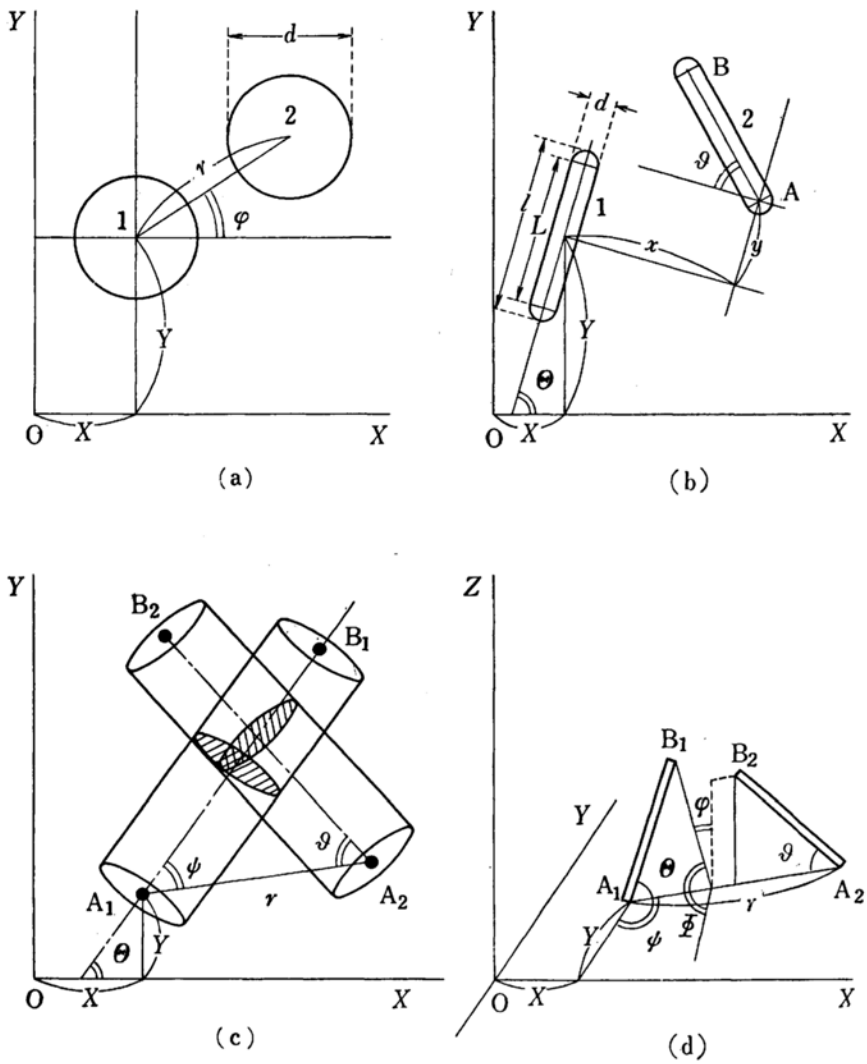

Fig. 1. Coordinate systems used in the cases of (a) $\theta=0°$; (b) $\theta=90°$; (c) $\theta=\theta_0$; and (d) θ is indefinite.

$$\int g_2\{2\}\,\mathrm{d}\{2\} = -\int_S \mathrm{d}X\mathrm{d}Y\int_0^{2\pi}\mathrm{d}\varphi\int_0^d r\,\mathrm{d}r$$
$$= -\pi S d^2 \qquad (15)$$

By combining this with Eq. 8, an equation exactly identical with Eq. 2 is obtained.

The Case in which All Molecules are Lying Flat upon the Interface ($\theta=90°$).—In order to avoid the complication arising from the overlapping of the edges of the rods, and to make the results of the present calculation comparable to the preceding results, the molecules are assumed to have round edges. To describe this shape of the molecule, it is assumed that a rod is composed of a circular cylinder of length L and diameter d and two hemispheres of diameter d at both ends of the circular cylinder, the center of the hemispheres being A and B, as shown in Fig. 1b.

When all rods are lying flat on the interface, the position and the orientation of a rod are designated by using three coordinates. For the three coordinates of rod 1, Cartesian coordinates X and Y of the center of gravity and the angle Θ between the X-axis and the axis of the rod may be used. For rod 2, the Cartesian coordinates x and y of the center of a hemisphere A (the origin of which is the center of gravity of rod 1 and the direction of the coordinate axes is perpendicular and

parallel to the direction of the axis of rod 1), and the angle ϑ between the axis of rod 2 and the coordinate axis $(-x)$ may be used as shown in Fig. 1b.

Then, $d\{2\}$ is $dXdYd\Theta dxdyd\vartheta$, $F_2\{2\}$ is $(1/4\pi^2)$ when two rods do not overlap with each other and is zero when they overlap, and $F_1\{1\}$ is $(1/2\pi)$. Therefore, the value of $g_2(1,2)$ is equal to $(-1/4\pi^2)$ when the rods overlap and is equal to zero when they do not. Therefore, the value of the integral calculated over the entire range of the coordinates corresponding to the overlapping of the rods is

$$\int g_2\{2\}d\{2\} = -(2S/\pi)(L^2+2\pi dL+\pi^2d^2/2) \tag{16}$$

This agrees with Eq. 15 if $L=0$. If the total length of the rod (that is $L+d$) is designated by l, and the value of A_0 is calculated from Eq. 8 by the aid of Eq. 16, then,

$$A_0=(1/\pi)l^2+2(1-1/\pi)dl+(\pi/2-2+1/\pi)d^2 \tag{17}$$

This agrees with Eq. 2 if $d=l$. Now, if the rods are very thin, $(d \ll l)$,

$$A_0 = (1/\pi)l^2 \tag{18}$$

The Case in which All Molecules are Inclined by the Same Angle($\theta=\theta_0$). — When all rods are inclined to the normal of the surface by the same angle θ_0, the position and the orientation of a rod may be specified by three coordinates. Fig. 1c shows the projection of rod 1 (A_1B_1) and of rod 2 (A_2B_2) onto the plane XY parallel to the interface. The three coordinates of rod 1 may be X and Y to give the location of the lower end A_1 of the axis and angle Θ to give the direction of the rod. The three coordinates of rod 2 may be r and ϕ to give the location of A_2 and ϑ to give the direction. Then, $d\{2\}$ is $dXdYd\Theta rdrd\phi d\vartheta$, and $g_2\{2\}$ is $(-1/4\pi^2)$ when two rods overlap and is zero when they do not.

The calculation of the range of overlapping is rather complicated in this case and needs some approximation. If the rods are sufficiently thin, rods 1 and 2 overlap with each other when $\vartheta=\phi$, and the height of the intersection h from the surface is $r/2\cos\phi\tan\theta_0$. Now, considering the rods of some thickness, the cross section of the rods will be an ellipse when the cross section is parallel to the interface. The range of the angle ϑ to give the overlapping of the ellipses at the hight of h will give the condition of the overlapping of the rods. It is not easy, however, to estimate this range of ϑ, because the mutual orientation of the ellipses depends on the value of r and ϕ. To avoid this mathematical complication, the ellipses will be replaced in this approximate calculation with circles of the same area. Then, the diameter of the equivalent circles d_0 will be $(d/\sqrt{\cos\theta_0})$ where d is the diameter of the rods. If the rods are sufficiently thin and long, that is, $2\sin\theta_0 > d_0/l$, the rods overlap approximately when

$$\phi-(2d_0/r)\cos\phi<\vartheta<\phi+(2d_0/r)\cos\phi \tag{19}$$

The final results thus obtained and applicable when $d/2l<\theta_0<\pi/2-d/l$ are

$$A_0=(\pi-4/\pi)d^2/2\cos\theta_0 + (\sin\theta_0/\sqrt{\cos\theta_0})dl \tag{20}$$

If $d \ll l$,

$$A_0=(\sin\theta_0/\sqrt{\cos\theta_0})dl \tag{21}$$

The Case in which Molecules can be Inclined at Any Angle with Equal Probability ($0<\theta<\pi/2$). — In this case, the position and the orientation of two rods 1 and 2 are defined by eight coordinates, X, Y, r, ϕ, Θ, ϑ, Φ and φ. As is shown in a perspective, Fig. 1d, X and Y give the position of A_1. r gives the distance between A_1 and A_2. ϕ gives the direction of A_1A_2. Θ gives the angle $B_1A_1A_2$. ϑ gives the angle $B_2A_2A_1$. Φ gives the angle between the plane $B_1A_1A_2$ and the plane XY. φ gives the angle between the plane $B_1A_1A_2$ and $B_2A_2A_1$. Here A_1 and A_2 are the lower end of rods 1 and 2, respectively, and B_1 and B_2 are the upper ends of rods 1 and 2. If the rods are sufficiently thin and $d \ll l$, the two rods overlap in the following three cases:

(1) $0<\Theta<\pi/2$, $0<\vartheta<\pi/2$, $0<r<l(\cos\Theta+\cos\vartheta)$ and $-(d/r)(1/\tan\Theta+1/\tan\vartheta) < \varphi < (d/r)(1/\tan\Theta+1/\tan\vartheta)$;

(2) $\pi/2<\Theta<\pi$, $0<\vartheta<\pi-\Theta$, $0<r<l(\cos\vartheta+\sin\vartheta/\tan\Theta)$ and $-(d/r)(1/\tan\Theta+1/\tan\vartheta) < \varphi < (d/r)(1/\tan\Theta+1/\tan\vartheta)$;

(3) $\pi/2<\vartheta<\pi$, $0<\Theta<\pi-\vartheta$, $0<r<l(\cos\Theta+\sin\Theta/\tan\vartheta)$ and $-(d/r)(1/\tan\Theta+1/\tan\vartheta) < \varphi < (d/r)(1/\tan\Theta+1/\tan\vartheta)$.

Then, by using the value of a definite integral, $\int_0^1(\tan^{-1}x/x)dx=0.9160$, the following equation can be obtained under the

assumption that $d \ll l$.

$$A_0 = 1.7014\, dl \qquad (22)$$

Eq. 22 corresponds to Eq. 21 with $\theta_0 = 71.8°$. This value of θ_0 is considered to be the statistically averaged value of θ for freely orienting molecules.

Applications for Gaseous Films of Fatty Acids

The theoretical equations derived above are to be applied to gaseous films and not to condensed films because multiple collisions, important in condensed films, are not taken into account in the derivations of these theoretical equations.

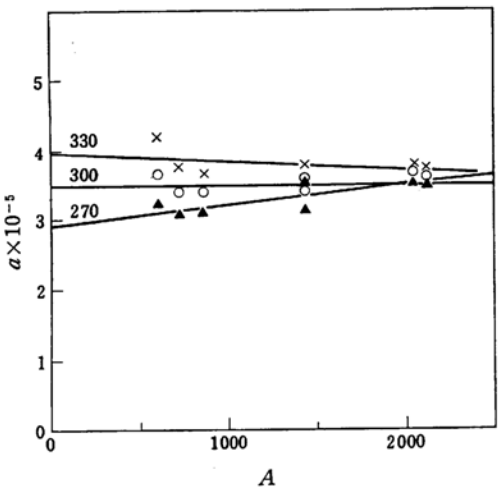

Fig. 2. The dependence of a on A for tridecylic acid, the parameter being A_0.

Therefore, the equations are applied to gaseous films of fatty acid using the experimental data given by Adam and Jessop[5]. In order to obtain the values of the constants a and A_0 of the van der Waals type equation, Eq. 1 was rewritten in the following form:

$$a = [kT/(A - A_0) - F]\, A^2 \qquad (23)$$

and the value of a for systematically varied values of A_0 are calculated by using experimental values of A and F given by Adam and Jessop. The value of a thus calculated for tridecylic acid are shown in Fig. 2. It is seen that the value of a is independent of A if the value of A_0 is assumed to be 300 Å^2. The values of a and A_0 thus obtained for tridecylic acid and myristic acid are shown in Table I.

TABLE I. CONSTANTS OF GASEOUS FILMS

	A_0	$a\times10^{-5}$	M	a/M^2	
Myristic acid	320	4.02	228	7.74	7.71
Tridecylic acid	300	3.52	214	7.68	

The data used for these calculations are shown in Fig. 3 with ○ for myristic acid and with △ for tridecylic acid. Curves in the figure shows the values calculated by Eq. 1, using the values of constants given in Table I. These curves explain well the experimental plots. Horizontal lines in the figure show where a two-dimensional phase change occurs. It is obvious that Eq. 1 does not hold over the pressure of the phase change.

As for the constant a, it is often said

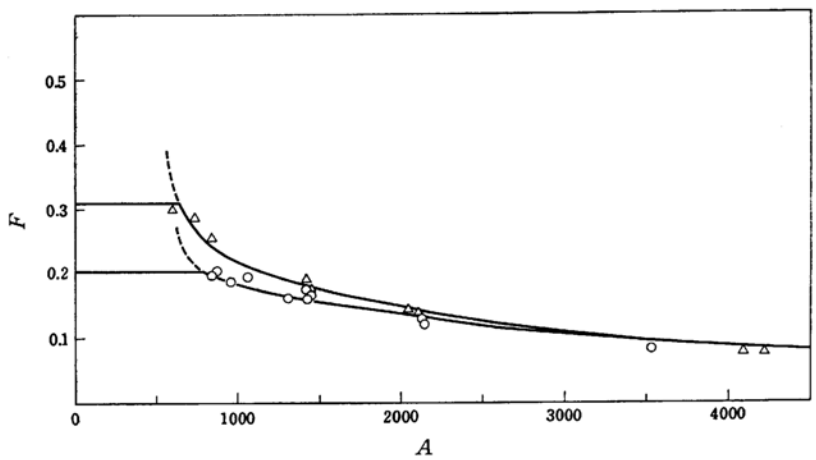

Fig. 3. Gaseous films of myristic acid and tridecylic acid.
○: Myristic acid △: Tridecylic acid

5) N. K. Adam and G. Jessop, *Proc. Roy. Soc.* (*London*), **A110**, 423 (1926).

that its value is proportional to the square of the molecular weight. This is valid in this case since the value of a/M^2 in Table I gives the relation,

$$a = 7.71 \times M^2 \qquad (24)$$

In order to compare the values of A_0 given in Table I with the theoretical equations derived above, the molecules are assumed to be rods of 5.0 Å in diameter and of $(6.0+1.3m)$ Å in length, where m is the number of carbon atoms in the hydrocarbon chain of the molecule. The values thus assumed are cited in Table II.

TABLE II. THE CONSTANT A_0 FOR GASEOUS FILMS

	d Å	l Å	A_0 $\theta=0°$ Å^2	A_0 $\theta=71.8°$ Å^2	A_0 $\theta=90°$ Å^2
Myristic acid	5.0	22.9	39.3	270	320
Tridecylic acid	5.0	21.6	39.3	258	294
Lauric acid	5.0	20.3	39.3	247	267

These values seem reasonable on the basis of various surface chemical studies and are compatible with the values already used by the present author[6]. Using these values of d and l, values of A_0 are calculated for vertical orientation, $\theta=0°$, by Eq. 2; for free orientation by Eq. 20 with $\theta_0=71.8°$; and for horizontal orientation, $\theta=90°$, by Eq. 17. The values thus calculated are shown in Table II. Comparing these with those in Table I, it may be concluded that the molecules of myristic acid and tridecylic acid are lying flat upon the interface.

In the case of lauric acid, the F–A curve obtained experimentally by Adam and Jessop is different from those of myristic and tridecylic acid, because lauric acid does not show any definite phase transition at the range of some hundred Å^2, as shown with ○ in Fig. 4. If it is assumed that the molecules of lauric acid are rods of $d=5.0$ Å and $l=20.3$ Å, and lying flat on the interface, A_0 should be 267 Å^2 as shown in Table II. On the other hand, a should be 3.08×10^5 for lauric acid according to Eq. 24. By using these values with Eq. 1, the solid curve in Fig. 4 is obtained. The curve can explain the experimental data to some extent in the region of larger A values, but the experimental data for smaller A values neither coincide with the van der Waals equation shown by the solid curve nor show any phase transition. The data will be explained by the assumption that the molecules at first lying flat on the interface gradually stand up according to the compression of the monolayer.

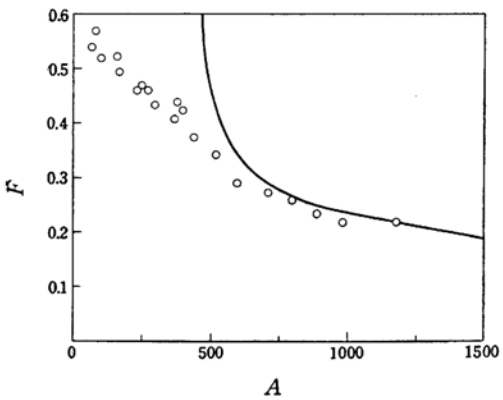

Fig. 4. Gaseous film of lauric acid.

Assuming that the molecules of lauric acid are rods of the above described dimensions, the value of A_0 is calculated as a function of the angle θ, that is the angle between the normal of the interface and the axis of the molecule. The curve in Fig. 5 is thus obtained by using Eqs. 2, 17 and 20. The point f in the figure shows the value of A_0 for the case in which the molecules can take any value of θ with equal likelihood.

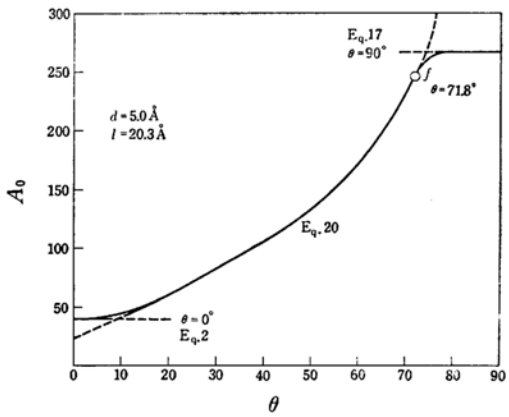

Fig. 5. The relationship between A_0 and θ for lauric acid.

By using, on the other hand, Eq. 1 together with the value of $a=3.08\times10^5$, the value of A_0 can be calculated as a function of the area A from the experimental data shown in Fig. 4. From this value of A_0, the value of θ can be obtained on the basis of Fig. 5. The relation between θ and A thus obtained are shown in Fig. 6. The horizontal line in the

6) M. Nakagaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 72, 113 (1951).

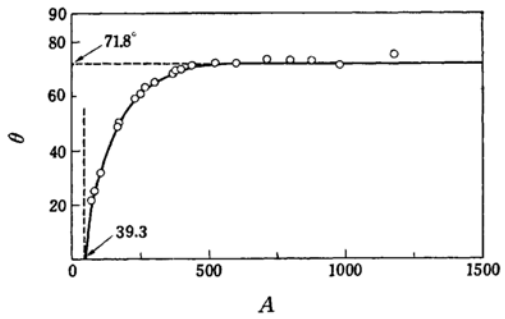

Fig. 6. The orientation of lauric acid molecules as a function of A.

figure shows the case of free orientation, in which the statistically averaged value of θ is 71.8°, and the vertical line shows the case in which all molecules are vertical to the interface. Molecules of lauric acid are in free orientation when the area A is very large, but the molecules interfere with each other and θ becomes smaller when A is les than about 500 Å^2. At last, all the molecules are vertical when A is 39.3 Å^2.

Summary

On the basis of the two-dimensional analogy of the method of McMillan and Mayer, the van der Waals constant A_0 for monolayers of rigid rod-like molecules is calculated theoretically for the cases in which all molecules are (1) vertical to the interface; (2) lying flat upon the interface; (3) inclined by a constant angle θ_0; and (4) orienting freely.

The theoretical equations thus obtained are used to discuss the orientation of molecules in gaseous films of myristic acid, tridecylic acid and lauric acid. As the results, it is concluded that the molecules of myristic acid and tridecylic acid are lying flat upon the interface in the gaseous film until the phase transition to a condensed film occurs. On the other hand, molecules of lauric acid are freely orienting when the area per one molecule is large, and the orientation becomes the more vertical, the more the monolayer is compresssed. The molecular orientations during this compression process were described quantitatively.

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