STUDIES OF MONOMOLECULAR FILMS BY THE RIPPLE METHOD. I.

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They say that the navigator, in former times, used to drop some oil into the sea from ship side to subside the breakers in the case of stormy weather.⁽¹⁾ The vegetable oil, such as linseed oil, is said to be most effective in this action. We undertook to study this phenomena.

At first, we made the wave by blowing the surface of water in a basin by an air blower. Then a small quantity of oil was dropped on the water surface, but the wave did not subside.

Next, we put the water basin on a thin wooden plate with a small electric motor side to side. Thus the vibration accompanied by the rotation of motor made fine stationary waves on the water surface of the basin. Now the surface is touched with a glass rod which is varnished with the oil, for example, oleic acid, then the wave subsides at once. This is a good lecture demonstration. If the initial water surface is contaminated with some dirty matter, then the experiment does not result well. The wave surface must sufficiently be clean and free from oily matter. It is advisable to sweep the water surface with a paraffined glass rod before the experiment is done.

Thirdly, we have made the ripple by means of a tuning fork, which is kept in contact with the surface of the water. The results obtained by this method is described in the following lines.

The action of the oil film on the ripple was first studied by Miss Pockels in 1891.⁽²⁾ Recently, Gorter and Seeder have developed this method and experimented on palmitic acid, lauric acid, casein and zein.⁽³⁾ We followed the method of Gorter and Seeder in our measurement.

Ripple was made by electrically-maintained tuning forks, whose vibrational numbers were 50, 100 and 200 per second respectively. The height of the wave was measured by means of the reflection of light on the waved surface. Fig. 1 is the schematic view of the measuring apparatus.

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(1) Marcelin, *Kolloid-Beiheft*, **38** (1933), 185.

(2) Miss Pockels, *Nature*, **43** (1891), 437.

(3) Gorter and Seeder, *Kolloid-Z.*, **58** (1932), 257.

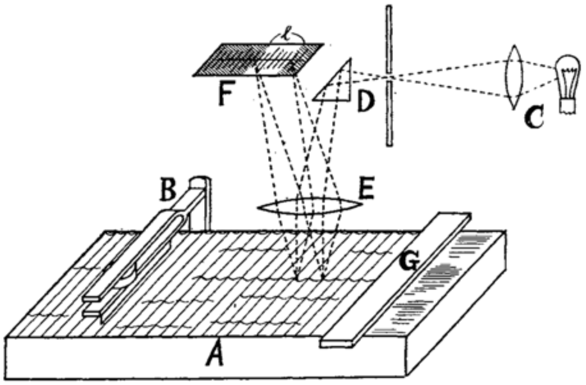

Fig. 1.

A is the water tray, the inner side of which is painted with paraffin. The wave is made by the tuning fork B. C, D, E shows the optical system by which a parallel light comes vertically on the water surface. The diffuse light reflected by the wave surface is now focused by the lens E on the scale F as a band of light. The width of the band, l, on the scale is nearly proportional to the amplitude of the wave, provided the amplitude is small compared with the wave length. G is a glass plate painted with paraffin and is used to change the surface area of water covered with oil film.

The "thickness" of the oil film, or the area of the single oil molecule is changed by two methods. The first method is as follows: A small quantity of the benzene solution of oil is put on the water and after the solvent has evaporated the wave is made and measured. Then the thickness of oil is changed by adding more and more oil (dissolved in benzene) successively and the measurements are done at every time. The area of the water surface is kept constant throughout. A tray of the size 14×20 cm.^{2} was used in this case. We shall call this method "the method of constant surface area".

Then the second method is as follows: A small quantity of the benzene solution of oil is put on the water surface, and after the benzene has evaporated the area of the oily surface is changed by glass slide G. A tray of 14×50 cm.^{2} was used in this case. We shall call this method "the method of constant oil quantity".

The area occupied by the single oil molecule, a, is calculated as usual, by dividing the area of water surface with the number of molecules of the spread oil. The width, l, of the band of reflected light on the scale E changes with the molecular area of oil, a. The relations between these two quantities have been measured.

The underlying water in the tray was sometimes alkaline and sometimes acidic according to the solubility of the oil in the water. The tap water of pH=8 is used as the alkaline water and the hydrochloric acid of 0.04 N as the acidic one.

Table 1 shows the observed data for palmitic acid spread on the alkaline water (pH=8) at 14°C., the constant surface area method being used. The vibrational frequency of the tuning fork was 100 per second. The area of the tray was 14×20 cm^2.

Table 1.

Quantity of palmitic acid (mg.)	Area per molecule α (Å^2)	Width of the band l (cm.)	Quantity of palmitic acid (mg.)	Area per molecule α (Å^2)	Width of the band l (cm.)
0		4.2	0.0348	34.0	3.45
0.0132	89.7	3.95	0.0375	31.6	2.9
0.0158	74.7	3.8	0.0400	29.6	1.0
0.0205	57.8	3.95	0.0436	27.2	0.5
0.0230	51.5	3.95	0.0463	25.6	0.3
0.0256	46.2	4.0	0.0478	24.8	0.34
0.0282	42.0	3.95	0.0504	23.5	0.32
0.0309	38.3	3.95	0.0543	21.8	0.30
0.0329	36.0	3.7	0.0582	20.3	0.30

Fig. 2 shows the curve of α against l. The value of α at the minimum point of l is 25.6 Å^2. We shall denote this point with α_m.

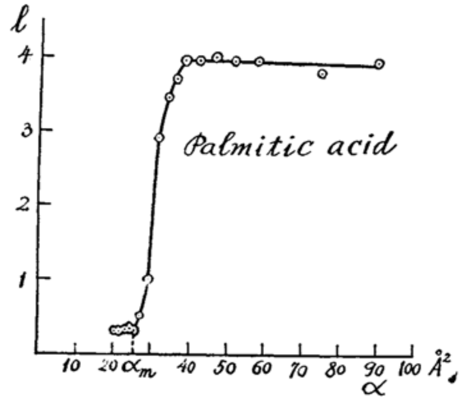

Fig. 2.

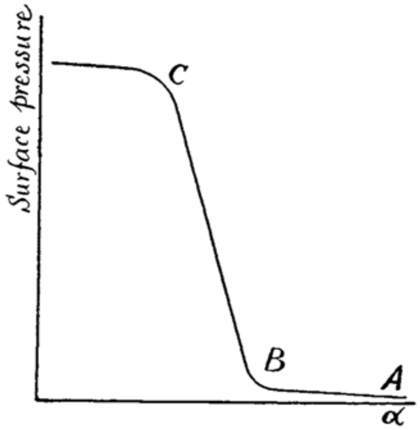

Fig. 3.

Now we shall consider the reason of the subsiding action of oil film on the water surface. The curve in Fig. 3 shows the general relation between the molecular area and the surface pressure of oil on water. In this curve the region AB corresponds to the gaseous film and BC the condensed film. In the portion AB the surface pressure is very small or the surface tension is nearly equal to that of the pure water. At point B the surface tension begins to show sharp decrease which continues until C.

It is probable that the subsiding action of wave is caused by the change of surface tension. In Fig. 4 the line *ace* shows the level of the water surface, and *abcde* the waved surface. The surface *abcde* is, of course, larger than the surface *ace*, so the oil film on the waved surface is thinner than that on the plane one. The surface tension of the waved surface is, therefore, larger than the plane one, and accordingly, the surface force will act to suppress the wave. Thus the decrease of the surface tension acts as the counterforce against the wave making action.

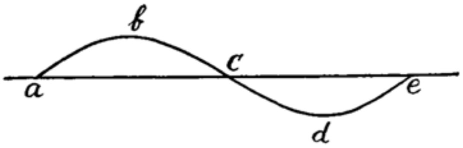

Fig. 4.

In the region AB in Fig. 3, the surface tension is almost independent of the molecular area, so the wave height does not differ from that of the clean water surface. If, however, the molecular area is smaller than the point B, the decrease of surface tension becomes significant and accordingly the wave will subside.

From the above consideration, we know that the point B in Fig. 3 corresponds to the point a_m in Fig. 2. The sectional area of the oil molecule is calculated, generally, by the surface pressure curve, assuming that the point B expresses the close packed monomolecular oil film. By the ripple method, therefore, the value of a_m will be the cross section of the oil molecule, for palmitic acid this being 25.6 Å^2.

The curves of l against a obtained on stearic acid, myristic acid, oleic acid, tetradecyl alcohol and palmitonitrile are given in Fig. 5, Fig. 6 and Fig. 7.

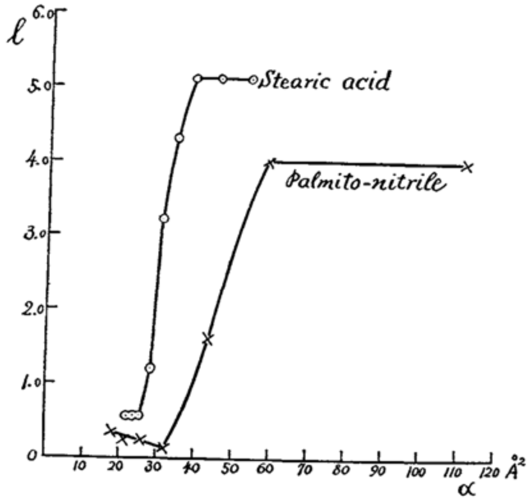

Fig. 5.

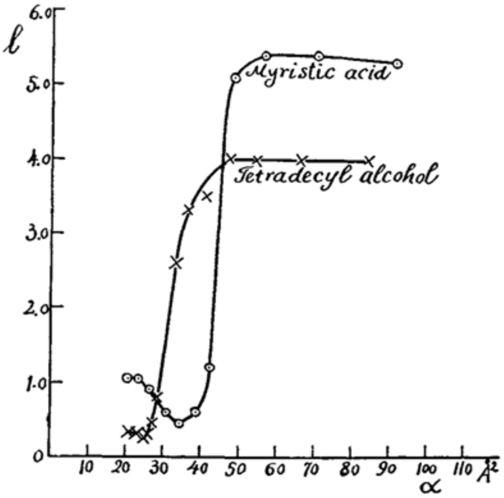

Fig. 6.

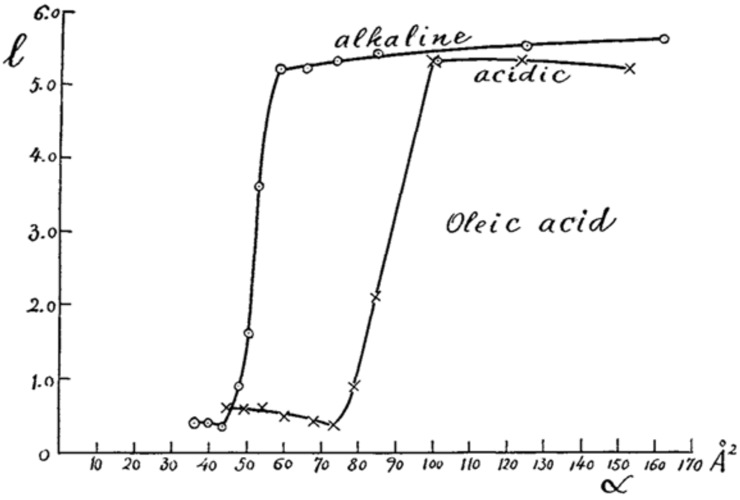

Fig. 7.

These curves have been obtained by the constant surface area method and the tuning fork of 100 vibrations. The results are summarised in Table 2. This table shows the film substances, temperatures, properties of the underlying water and the values of a_m obtained. Moreover, in the last column, the values of the cross sectional areas of the molecules are given which were calculated from the surface pressure curves by other authors.

Table 2.

Substance	Temperature (°C.)	Underlying water	α_m (Å^2)	Molecular area (Å^2)	Author
Palmitic acid	14	alkaline (pH=8)	25.6	21	Langmuir(4)
Stearic acid	14	alkaline (pH=8)	25.8	22	Langmuir
Myristic acid	5	alkaline (pH=8)	34.6	21 (condensed film) 40.6 (expanded film)	Adam(5)
Oleic acid	14	alkaline (pH=8)	43.7	46	Langmuir
Oleic acid	13	acidic (0.04 N HCl)	74.0		
Tetradecyl alcohol	17	alkaline (pH=8)	25.1	21.6	Adam
Palmitonitrile	12	alkaline (pH=8)	32.9	27.7	Adam

From this table we see that the values of α_m are nearly equal to the values of molecular area obtained by Langmuir and Adam, excepting the oleic acid film on the acidic water. The molecules of the acidic substances have less affinity with the acidic underlying water than the alkaline one. So the oil molecules may be in active motion, or float in inclined state instead of vertical position. The value of α_m, therefore, becomes larger in this case than the case of alkaline underlying water. This fact will be discussed further in the second paper of the present investigation.

We shall now study the effect of the vibrational number of the tuning fork. According to the theory of hydrodynamics there is the following equation.

$$v^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\gamma}{\rho\lambda}$$

where v denotes the velocity of propagation of the wave, g the gravity constant, λ the wave length, γ the surface tension and ρ the density of liquid. The first term of the light side of this equation gives the effect of gravitational force and the second term that of the surface tension.

In the present experiment, if the vibrational number of the tuning fork is large the wave length λ will be small and the first term of the equation becomes negligible. In such a case the height of the wave is mainly governed

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(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848.

(5) Adam, *Proc. Roy. Soc.*, A, **101** (1922), 452; **103** (1923), 687; Adam and Dyer, *Proc. Roy. Soc.*, A, **106** (1924), 694.

by the surface tension, and the wave will be subsided by the change of surface tension. If, however, the vibrational number of the tuning fork is small, the wave will not be subsided by the surface action only, but will have a residual wave of considerable height at the point a_m. We have tested the relations between the damping effect of film and the wave length by using the tuning forks of 50, 100 and 200 vibrations per second. Table 3 gives the percentage ratios of the height of the residual wave to that of the undamped one.

Table 3.

Vibration number of tuning fork per second	50	100	200
Palmitic acid	27%	7.5%	3.7%
Myristic acid	38	8.4	3.3
Oleic acid	23	7.4	3.3
Palmitonitrile	19	5.0	4.2

From Table 1 and Fig. 2, for example, the readings of the widths of the band l, for palmitic acid in using 100 vibration fork are taken. In this case, the value of l of damped wave (at a_m) and that of undamped one are 3 mm. and 40 mm. respectively, being given as 7.5% in Table 3. We see, from this table, that the height of the residual wave decreases with the increase of vibrational number. Thus the larger the vibrational frequency, the more predominant the capillary wave.

Now we shall consider the subsiding action of oil for the breaker in the ocean. The high wave in the ocean is not, of course, the capillary one, so the action of oil may not, directly, be explained by the mechanism described above. But we may understand the damping action of the oil for breakers in ocean in the following manner.

The high wave is produced, mainly, by the action of wind. If there is no ripple in the water surface, then the wind will pass along the surface without any appreciable resistance. If, however, the water surface is not smooth but full of ripples, then the resistance between the water surface and the air current will be large and, accordingly, the breakers will appear. Thus the ripple is considered to be the cause of the breaker. The oil film has the subsiding action on the ripples as has been described in this paper. So the oil film will decrease the resistance between the wind and the surface, and consequently, the breaker will no more appear.

The present experiment has been done by the fund of Nippon Gakujutsu Shinkokwai (Foundation for the Promotion of Scientific and Industrial Research of Japan) for which the authors' sincere thanks are due. Some of the substances used in the experiment were synthesized by Professor Kubota and other members in the organic laboratory of our institute to whom the authors express their gratitude.

Summary.

(1) The change of height of the capillary wave by the oil film has been measured, "the constant surface area method" being used. The substances tested are palmitic acid, stearic acid, myristic acid, oleic acid, tetradecyl alcohol, and palmitonitrile.

(2) The area per molecule of oil has been calculated for which the capillary wave subsides, and this has been compared with the cross sectional area of molecules obtained by other authors.

(3) The effect of the change of vibrational number on the subsiding action of wave has been studied.

(4) The mechanisms of the subsiding action of oil film on the capillary wave and the breaker have been described.

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