STUDIES OF MONOMOLECULAR FILMS BY THE RIPPLE METHOD. II.

By **Tsunetaka SASAKI** and **Jitsusaburo SAMESHIMA.**

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In the preceding paper we have described the results obtained by the "method of constant surface area".⁽¹⁾ In the present report, the experiments are described on the "method of constant oil quantity".

The total area of the water tray is 14 × 50 cm.^{2}, and the effective area can be changed by moving a glass strip (Fig. 1 in the preceding paper). The wave is made by an electrically maintained tuning fork of 100 vibrations per second. Known quantity of oil (dissolved in benzene) is put on the water surface and the wave height is measured as was described in the preceding paper. Now the surface area is changed by moving the glass strip, the oil film being compressed or expanded, and the wave height is measured every time.

Fig. 1 shows the general type of the curves of the molecular area, a, against the wave height, l. The curve *acd* corresponds to the compression of the film, starting from a, passing a minimum point c and reaching d. The curve *deb* corresponds to the expansion of the film. At the point e the wave begins to appear and its height increases to b. Thus there occurs a hysteresis phenomena.

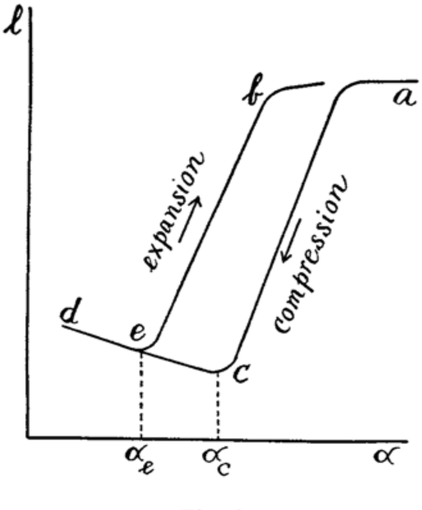

Fig. 1.

Table 1 shows the data obtained on the oleic acid. The quantity of the oleic acid dispersed on the surface is 0.0000292 gram. The temperature is 15°C., the underlying water is acidic (0.05 N HCl) and the vibration frequency of the tuning fork is 100 per second. The data are plotted in Fig. 2.

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(1) Sameshima and Sasaki, this Bulletin, **11** (1936), 539.

Table 1.

Compression			Expansion		
Surface area (cm.^{2})	Area per molecule α (Å^2)	Width of the band l (cm.)	Surface area (cm.^{2})	Area per molecule α (Å^2)	Width of the band l (cm.)
560	89.4	5.0	238	38.0	0.8
532	84.9	4.8	252	40.2	0.75
504	80.4	4.5	266	42.4	0.75
476	76.0	4.0	280	44.7	0.70
448	71.5	3.1	294	46.9	0.65
392	62.6	1.1	308	49.2	0.65
378	60.3	0.7	322	51.4	0.95
364	58.1	0.4	336	53.6	1.4
350	55.9	0.45	350	55.9	2.4
336	53.6	0.55	364	58.1	3.1
322	51.4	0.7	392	62.6	3.3
308	49.2	0.7	448	71.5	4.7
294	46.9	0.72	476	76.0	5.2
280	44.7	0.70	504	80.4	5.3
266	42.4	0.75	532	84.9	5.3
252	40.2	0.75			
238	38.0	0.8			
224	35.7	0.9			

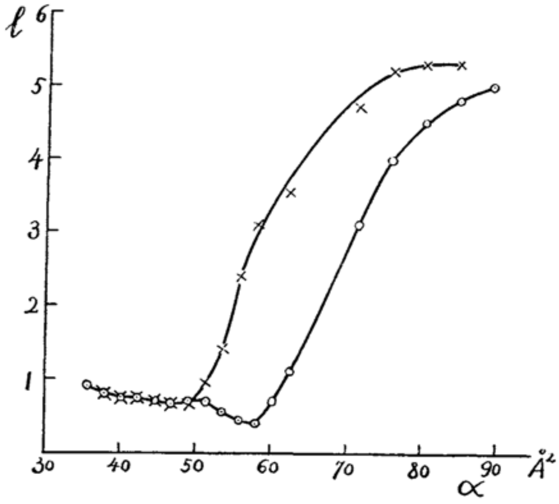

Fig. 2.

Similar results have been obtained on palmitic acid, myristic acid, tetradecyl alcohol and palmitonitrile. The hysteresis phenomena were observed by Langmuir in the measurement of suface pressure.(2)

We shall consider the meaning of the curves of Fig. 1. In the film the polar group in the oil molecule is attracted by the underlying water, and therefore, the oil molecule is considered to stand vertically at the surface of the water. The affinity, however, between the acid oil and the water is smaller in the case of the acidic water than in the case of alkaline one. So when the underlying water is acidic and the surface area is sufficiently large, some of the molecules may be in the inclined state, instead of vertical. The surface film of such a state is now compressed until the oil molecules are in contact with one another, forming a monomolecular film. This state corresponds to the point c in Fig. 1 and is pictured schematically in Fig. 3A. The capillary wave subsides at this point. On further compression the oil molecule will stand up gradually until all in vertical position as shown in Fig. 3B, and then follows the usual compression behavior of the monomolecular film.

Fig. 3.

Now we enlarge the surface of water by moving the barrier in the opposite direction, and let the film expand. At the point e in Fig. 1 the wave begins to appear and its height increases gradually until the point b. The point e corresponds to the state of Fig. 3B, i.e. the monomolecular film of the uncompressed state. All the oil molecules are in vertical position at this point. The point e, therefore, corresponds to the point a_m in Fig. 2 of the preceding paper.

The values of the area of a single molecule α at the kink point e in the expansion curve and c in the compression one are given in Table 2. The vibrational frequency of the tuning fork is 100 per second.

Table 2.

Film substance	Underlying water	Temperature (°C.)	Values of α at the kink point of the curve of	
			compression α_c (Å^2)	expansion α_e (Å^2)
Oleic acid	acidic (0.05 N HCl)	15	58	49
Palmitic acid	acidic (0.05 N HCl)	11	29	25
Myristic acid	acidic (0.05 N HCl)	12.5	57	52
Tetradecyl alcohol	alkaline (pH=8)	17	35	23
Palmitonitrile	acidic (0.05 N HCl)	11	39	32

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(2) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1874.

The values of a_e at the kink point of the curve of expansion are thus nearly identical with the values of a_m obtained from the "method of constant surface area", given in Table 2 in the preceding paper.

In the case of myristic acid the value of a_e is 52 Å^2 at 12.5°C., while a_m is 34.6 Å^2 at 5°C. The myristic acid forms an expanded film at 12.5°C., but a half condensed film at 5°C., so the molecular area differs in these two temperatures. When the underlying water is alkaline, the film dissolves into the water and the definite kink point is not obtained.

The compression curve has not been drawn for the substances shown in Table 3. The expansion curves have been measured, and therefore, only the values of a_e are given in the table.

Table 3

Film substance	Underlying water	Temperature (°C.)	Molecular area from the expansion curve α_e (Å^2)
Lauric acid	acidic (0.05 N HCl)	14	47
Tripalmitin	acidic (0.05 N HCl)	13	71
Triolein	acidic (0.05 N HCl)	12	138
Ricinoleic acid	acidic (0.05 N HCl)	12	91
Ethyl palmitate	acidic (0.05 N HCl)	12	65

The above are the results of measurements on the substances of known molecular weight. In these cases, thus, we can know a sectional area of the molecule by the ripple method. If, however, a substance of unknown molecular weight is used, the approximate magnitude of its molecular weight may be calculated. The experiment has been done on mastic.

The selected sample of mastic is dissolved in ethyl alcohol, filtered and then diluted with benzene. The solution thus obtained is put on the water surface of the tray. The solution spreads and the alcohol and benzene soon evaporate, the film of mastic remaining on the surface. The quantity of mastic dissolved in the solution is determined by evaporating the solvents at 110°C. and weighing the residue. Table 4 and Fig. 4 show the results of maesurements on mastic.

Table 4.

Weight of mastic (g.)	Area of the film (cm.^{2})	Width of the band l (cm.)
6.25×10^{-5}	280	0.4
	294	0.4
	308	0.3
	322	0.25
	336	0.3
	350	1.2
	364	3.2
	378	4.2
	392	4.6
	420	5.0

Weight of mastic (g.)	Area of the film (cm.^{2})	Width of the band l (cm.)
6.54×10^{-5}	280	0.3
	294	0.3
	308	0.3
	322	0.3
	336	0.3
	350	0.1
	364	0.2
	378	0.9
	392	2.6
	406	3.6
	420	4.1.
	448	4.6
	476	4.7

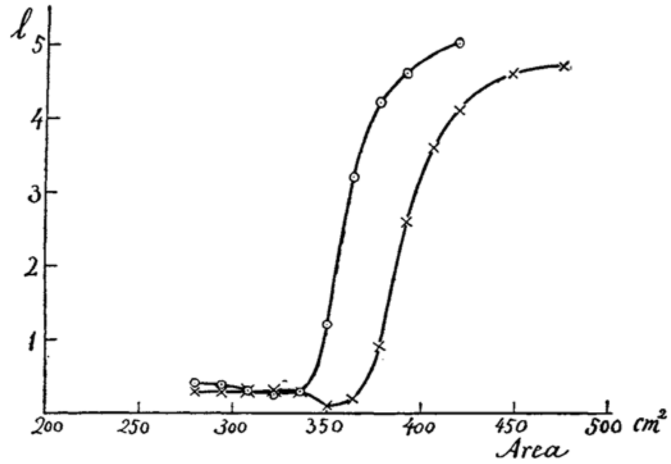

Fig. 4.

From Fig. 4 we see that the wave subsides at the film area of 330 cm.^{2} in the first experiment, and 350° cm.^{2} in the second one.

The molecular weight of mastic is not known, so the area per molecule cannot be calculated. We shall assume that the mastic molecule has the cubic form, and calculate its molecular weight.

Let us denote with g the weight of mastic spread on the water surface, and s the area of film where the wave subsides, and d the density of mastic, then the thickness of the film will be expressed by g/sd. The diameter of the single molecule is assumed to be equal to the thickness of the film, and the volume of single molecule is $(g/sd)^3$. The molecular weight is expressed by,

$$M = \left(\frac{g}{sd}\right)^3 Nd = \frac{Ng^3}{s^3d^2}$$

where N denotes the Avogadro number.

In the present experiment, the density of the mastic has been found to be $d = 1.058$. The value of the molecular weight calculated from the results of the first experiment is as follows:

$$M = \frac{6.06 \times 10^{23} \times (6.25 \times 10^{-5})^3}{330^3 \times 1.058^2} = 3678.$$

The same from the second experiment is:

$$M = \frac{6.06 \times 10^{23} \times (6.54 \times 10^{-5})^3}{350^3 \times 1.058^2} = 3532.$$

Taking the means, we have the value 3605. Thus the molecular weight of mastic has been found to be about 3600.

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 oil quantity method" being used. The substances tested are oleic acid, palmitic acid, myristic acid, tetradecyl alcohol, palmitonitrile, lauric acid, tripalmitin, triolein, ricinoleic acid, and ethyl palmitate.

(2) It has been found that there occurs some hysteresis phenomena in the subsiding action of the capillary wave by compression and expansion of the film.

(3) The areas per molecule of oils have been calculated from the kink point in the expansion curve of the film.

(4) Experiments have been done on mastic, the molecular weight of which being estimated at about 3600.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.