STUDIES ON THE OILINESS OF LIQUIDS. II. FRICTION COEFFICIENTS OF THE FILMS OF MONO- AND POLY-MOLECULAR LAYERS.

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Received September 29th, 1936. Published December 28th, 1936.

It is well known that the friction between two solid surfaces greatly diminishes by the presence of a small amount of greasy matter at the sliding surfaces. Hardy found that the value of the coefficient of friction is practically independent of the quantity of the lubricating liquid, or the thickness of the film of liquid.(1) Langmuir devised a method of depositing monomolecular film of oleic acid on a glass plate.(2) The friction coefficient of a glass reduces considerably by the presence of such a monomolecular film. Recently, this method has been improved by Blodgett and was made possible to deposit successive layers of fatty acid on a solid surface.(3) The method is as follows. Let a small quantity of the fatty acid spreads on the surface of the water making monomolecular film. The area of the film is confined by using a boundary thread and a "piston oil" of oleic acid. Now a glass plate is dipped edgewise in such a water and withdrawn slowly, then a monomolecular film of fatty acid will be deposited on the glass plate. If this glass plate is dipped into the water again and withdrawn, then there deposit two more layers, the plate being covered with three molecular layers of fatty acid. If the process is repeated once more, then the number of layers becomes to five and so on.

By this method, we have made the films of known thickness on a glass plate, and have measured the coefficient of static friction of such a glass surface. The method of measuring of the static friction coefficient has already been described in the preceding report.(4) The plate and the slider were cleaned by heating in chromic mixture for more than one hour, washing with soap solution, linsing in running water and then drying in a current of the clean air. A microscope slide-glass was used as the sliding surface, and a watch glass as the slider. Blodgett's method has been conducted under the following conditions. The tap water was used for the underlying water of monomolecular floating film, the hydrogen concentration of which being

(1) Hardy and Doubleday, *Proc. Roy. Soc.* (London), A, **100** (1922), 550.
(2) Langmuir, *Trans. Faraday Soc.*, **15** (1920), 68.
(3) Blodgett, *J. Am. Chem. Soc.*, **57** (1935), 1007.
(4) Sameshima, Kidokoro, and Akamatu, this Bulletin, **11** (1936), 659.

pH = 7.8 and containing some calcium ion. As the "piston oil" we used the oleic acid or the castor oil. The experiments were done at the room temperature.

The slide-glass was made clean by the above method, and one half of the surface was covered with the film of known thickness by Blodgett's method. The coefficients of friction were measured on the clean part and on the part covered with film. An actual example is shown in Table 1.

Table 1.

Surface of plate	Surface of slider	W (g.)	F (g.)	μ	Mean
Clean glass	Clean glass	20.6 25.1 29.3 31.4	25.52 23.08 29.48 34.40	1.24 0.92 1.00 1.10	1.04
Glass covered with the film of stearic acid of 1-molecular layer	Clean glass	25.1 26.5 29.3 31.4	3.15 2.72 2.70 3.59	0.13 0.10 0.09 0.11	0.11
The same of 3-molecular layer	Clean glass	20.6	2.41	0.12	

In this table are shown the conditions of surfaces of the plate and the slider, the weight of the slider, W, the tangential force acting to the slider, F, and the coefficient of friction, $F/W=\mu$.

The value of μ, thus, reduces to about one tenth by the existence of the monomolecular layer of stearic acid. This value, however, does not noticeably change by the increase of the thickness of film from 1-molecular to 3-molecular layer.

We have measured, in the next place, the coefficient of friction when the contact surface of the slider was covered with the monomolecular layer of stearic acid. The results are shown in Table 2.

From Table 1 and Table 2 we see that the value of μ is somewhat larger when the slider is covered with film and the plate is clean, than the case of the clean slider and covered plate. The slider surface is in contact with the plate at a very small area if not at a point. So the monomolecular film of stearic acid on the slider is liable to be torn off at this contact point, and in consequence of this the friction becomes large. It is necessary, therefore, to deposit the film on the surface of plate in the study of the oiliness of films.

Table 2.

Surface of plate	Surface of slider	W (g.)	F (g.)	μ	μ Mean
Clean glass	Glass covered with the film of stearic acid of 1-molecular layer	26.2	8.53	0.33	0.34
		26.8	8.03	0.30	
		28.5	11.10	0.38	
Glass covered with the film of stearic acid of 1-molecular layer	Glass covered with the film of stearic acid of 1-molecular layer	25.7	2.42	0.09	0.11
		26.8	2.97	0.11	
		28.5	3.49	0.12	

The results of the measurements are summarized in Table 3. The data in this table have been obtained when the surface of plate is covered with the monomolecular film of the substances, the slider surface being clean. The "piston oil" used in the deposition of the film is also shown in the table.

From Table 3 we see that there are little differences of the coefficients of friction among these substances, provided that the thickness of film is 1-molecular. If the "piston oil" is changed from castor oil to oleic acid, there occurs, generally, a small change in the value of μ. Castor oil gives larger value of μ than oleic acid. This may be explained by the fact that oleic acid has greater surface pressure (about 30 dynes) than castor oil (about 17 dynes), so the former deposits the film in more compressed state than the latter.

Relatively large difference of μ is detected by the change of "piston oil" in the case of myristic acid. Myristic acid makes an expanded film and the compressibility of the film is larger than the other substances which make the condensed film.

The friction coefficients of the films thicker than 3-molecular layer are given in Table 4 and Table 5. The measurements have been done on palmitic acid and oleic acid. Oleic acid has been used for the "piston oil" in the deposition of films.

We see, from these tables, that there is almost no change in the value of μ, in spite of the change of thickness of the film. The presence of the film

Table 3.

Film substance	"Piston oil"	W (g.)	F (g.)	μ	μ Mean
Stearic acid	Castor oil	24.5	2.90	0.12	0.12
		25.1	3.15	0.13	
		31.4	3.59	0.11	
		32.8	3.68	0.11	
	Oleic acid	26.5	2.72	0.10	0.10
		29.3	2.70	0.09	
Palmitic acid	Castor oil	21.2	2.68	0.13	0.13
		26.7	3.15	0.12	
		30.9	3.53	0.11	
		31.0	4.31	0.14	
	Oleic acid	25.4	2.55	0.10	0.10
		29.0	2.75	0.09	
Myristic acid	Castor oil	22.6	4.71	0.21	0.20
		25.8	5.66	0.22	
		26.8	4.42	0.17	
	Oleic acid	21.9	2.65	0.12	0.11
		28.0	3.06	0.11	
		31.8	3.26	0.10	
Lauric acid	Castor oil	21.8	3.82	0.18	
	Oleic acid	25.1	4.54	0.18	0.18
		25.6	4.65	0.18	
Oleic acid	Castor oil	22.7	5.25	0.23	0.20
		26.6	4.78	0.18	
	Oleic acid	21.6	3.70	0.17	0.14
		21.6	2.39	0.11	
		24.3	4.28	0.18	
		24.3	2.15	0.09	
		32.1	4.27	0.13	
Ricinoleic acid	Castor oil	23.8	3.45	0.15	
	Oleic acid	25.5	3.00	0.12	0.12
		31.2	3.70	0.12	
Tripalmitine	Castor oil	20.9	3.12	0.15	0.14
		27.5	3.68	0.13	

Table 4.

Palmitic Acid Film.

Thickness of the film	W(g.)	F(g.)	μ	μ Mean
No film	(Table 1)			1.04
1-Molecular layer	(Table 3)			0.10
3-Molecular layer	25.4	2.66	0.11	0.09
	25.6	1.76	0.07	
	30.6	3.33	0.11	
	31.0	2.06	0.07	
5-Molecular layer	25.6	1.37	0.05	0.07
	27.5	2.10	0.08	
	29.0	2.26	0.08	
7-Molecular layer	23.3	1.30	0.06	0.06
	36.9	2.34	0.06	
9-Molecular layer	31.5	1.95	0.06	
11-Molecular layer	25.6	1.73	0.07	

Table 5.

Oleic Acid Film.

Thickness of the film	W(g.)	F(g.)	μ	μ Mean
No film	(Table 1)			1.04
1-Molecular layer	(Table 3)			0.14
3-Molecular layer	26.6	2.52	0.09	0.10
	26.6	2.43	0.09	
	29.1	3.70	0.13	
5-Molecular layer	25.3	3.54	0.14	0.16
	31.0	5.93	0.19	
7-Molecular layer	25.7	3.83	0.15	
9-Molecular layer	33.7	6.19	0.18	

of only 1-molecular layer reduces the friction coefficient to about one tenth of the clean glass surface, but no further reduction takes place by the increase of the thickness of film. This is a remarkable fact. In the film deposited by Blodgett's method, all of the oil molecules take the vertical position on the glass surface. The polar group of the oil molecule contacts with the surface of glass, and the nonpolar hydrocarbon group directs to the air. It is possible that such a regular arrangement of molecules favours the lubricating power more than the irregular arrangement. We can deposit the film on glass surface by means of the condensation of vapour or the evaporation of solvent from the solution. These methods, however, give less regular arrangement of molecules than Blodgett's method. On oleic acid the value of μ was measured to be about 0.3 in the case of the film deposited by the evaporation of the benzene solution. In the preceding paper, we reported that the value of μ of oleic acid is 0.29 when the glass surface is flooded with the liquid oil. Thus we see that the regular arrangement of oil molecules gives smaller friction coefficient than the irregular arrangement.

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' thanks are due.

Summary.

(1) The static friction coefficients have been measured when the monomolecular films of some fatty acids, etc. are deposited on glass surface.

(2) The static friction coefficients have been measured on palmitic acid and oleic acid, when the film thickness increase from one to several molecular layers.

(3) The friction coefficient of the monomolecular film is about one tenth of that of the clean glass surface. The value shows no further reduction by the increase of the thickness of film.

(4) Regular arrangement of oil molecules in the film gives lower friction coefficient than the irregular one.

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