Studies on the Oiliness of Liquids. X. The Friction Coefficients of Mono- and Multi-molecular Layers.*

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In one of the preceding papers of this series, the static friction coefficients of glass surfaces on which monomolecular and multimolecular layers of some long chain fatty acids such as palmitic or oleic acid were deposited, had been reported⁽¹⁾. The friction coefficients of glass surfaces lubricated with such films are about one tenth of that of clean glass. These low friction coefficients were ascribed to the regular arrangement of the molecule. In the present experiment, the friction coefficients of some long chain compounds and cholesterin were measured and the effects of various conditions were also studied.

The friction coefficients were measured by the balance method. The experimental procedure and cleansing of the glass surfaces are quite the same as described in the former papers.⁽²⁾ The deposition of the monomolecular and multimolecular layers of such long chain compounds on the glass surface were conducted by Langmuir-Blodgett's technique.⁽³⁾ When no indication is made, tap water was used as the substrate water which was regulated its pH value to about 9 by the addition of a small quantity of ammonia. The results are summarized in Table 1. The piston oil used in the deposition of the film is also indicated in the table.

Acids show low friction coefficients, while alcohols show relatively high friction coefficients. Moreover, the values of friction coefficients of alcohols, and ester fluctuate considerably, especially in the cases of tetradecyl and cetyl alcohol. In the table, only the two extreme values were recorded. When the film of long chain acid such as stearic acid was deposited on the glass surface by withdrawal of the glass plate from the water covered with monomolecular film, water is entirely repelled from the glass surface. On the other hand, when the film of alcohol or ester was deposited in the same way, the glass plate was wetted by water. If the glass plate was withdrawn too slowly out of the water surface, the film may slip down from the plate on the water surface. By the withdrawal of the moderate speed the film was transfered on the glass with water and this was dried in desiccator by passing the current of dry air, and used for the friction measurement. By this procedure, the arrangement of the molecules in the deposited film may be irregular. This is a reason of the high friction coefficient and its fluctuation.

The friction coefficient of oleic acid is 0.20 when castor oil was used as the piston oil⁽¹⁾ and somewhat higher than that of elaidic acid. The

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* IX, this Bulletin, **15** (1940), 288.

(1) H. Akamatu and J. Sameshima, this Bulletin, **11** (1936), 791.

(2) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659.

(3) K. Blodgett, *J. Am. Chem. Soc.*, **57** (1935), 1007.

Table 1.

Clean glass: $\mu = 1.04$

Film substance	Piston oil	μ	μ Mean
Elaidic acid	Castor oil	0.10 0.12 0.12 0.13 0.10 0.14 0.10 0.13 0.10	0.12
Myristic acid	Castor oil	0.18 0.20 0.14 0.22 0.18	0.18
	Oleic acid	0.12 0.12	0.12
Linolic acid	Castor oil	0.11 0.15 0.10	0.12
	Oleic acid	0.13 0.09 0.11	0.11
Brassidic acid	Castor oil	0.12	
	Oleic acid	0.11 0.10	0.11
Erucic acid	Castor oil	0.12 0.10 0.11 0.14	0.12
Cerotic acid	Castor oil	0.20 0.13 0.17 0.12	0.16
	Oleic acid	0.17 0.14 0.17	0.16
Triolein	Castor oil	0.20 0.18 0.16 0.17	0.18
Myricyl alcohol	Oleic acid	0.17 0.18 0.19 0.17 0.16	0.17

Table 1.—(*Concluded*)

Film substance	Piston oil	μ	μ Mean
Cholesterin	Castor oil	0.22 0.21 0.21	0.21
	Oleic acid	0.22 0.22	0.22
Tetradecyl alcohol	Castor oil	0.23~0.45	
	Oleic acid	0.19~0.47	
Cetyl alcohol	Castor oil	0.25~0.50	
	Oleic acid	0.18~0.52	
Octadecyl alcohol	Castor oil	0.18~0.34	
	Oleic acid	0.17~0.32	
Methyl palmitate	Castor oil	0.37~0.46	
	Oleic acid	0.32~0.46	

structure of the oleic acid is a cis-form while that of elaidic acid is a trans-form. Elaidic acid can be more closely packed than oleic acid. This fact may be a reason of the different friction coefficients of these two acids which have the same molecular formula. However, brassidic and erucic acid show almost the same friction coefficient. In the films of acids which are solid in ordinary temperature, the arrangement of the molecules is more regular than in that of liquid acids when the films are deposited in compressed state. This fact is a probable reason why oleic acid shows a relatively high friction coefficient. Cholesterin film shows the friction coefficient of the order of that of oleic acid.

In the former communication, it had been also reported that no further reduction of friction coefficient was observed by the increase of thickness of the film. However, in the present experiment it was found that the reduction of friction coefficient is caused definitely by the increase of the thickness of film. The friction coefficient diminishes gradually down to the penta- or heptamolecular layers, and then no further reduction could be recognised. Table 2 and Fig. 1 show the results. Oleic acid is only an exception. This is caused by the liquid nature of the substance in an ordinary temperature. When the number of layers are built up, assemblage of molecules in the film gains gradually the nature of liquid and the orientation of molecules in the film becomes somewhat more ir-

Table 2. μ of multimolecular layers.

Number of layers	Stearic acid	Oleic acid	Brassidic acid	Erucic acid	Palmitic acid
1	0.12	0.14	0.11	0.12	0.10
3	0.09	0.12	0.08	0.08	0.09
5	0.06	0.14	0.07	0.08	0.07
7	0.06	0.15	0.08	—	0.06
9	0.06	0.17	0.08	—	0.06
11	—	—	—	—	0.06

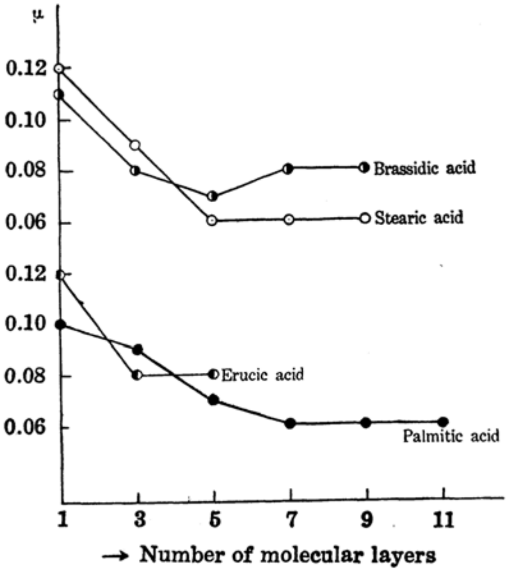

Fig. 1.

regular, so that the friction coefficient of oleic acid increases. Germer and Storks⁽⁴⁾ found by the examination of monomolecular and multimolecular layers with electron diffraction that on a clean metal surface molecules of the first layer stand with the axes of the hydrocarbon chains normal to the surface and the chains closely packed together laterally but irregularly arranged whereas in layers on top of the first, molecules of barium sterate or of stearic acid are regularly arranged. Accordingly, the fact that the friction coefficients of multimolecular layers being lower than that of monomolecular layers can be ascribed to more regular arrangement of the molecules in the film.

The effect of compression of the film by some piston oils of different spreading pressures during the deposition of film on the glass is also investigated. The results which were obtained by using oleic acid and castor oil as piston oil are shown partly in Table 1. The low pressure piston oils were prepared according to the indication of Norris and Taylor.⁽⁵⁾ The mixtures of various compositions of ethyl myristate and liquid paraffin which was specially purified for this purpose, were used. The spreading pressures were measured by Adam-Jessop's surface balance, and shown in Table 3. With these piston oils the effect of compression were studied. The results are shown in Table 4.

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(4) Germer and Storks, *J. Chem. Phys.*, **6** (1938), 280.
(5) Norris and Taylor, *J. Chem. Soc.*, **1938**, 1719.

Table 3.

Piston oil	% of ethyl myristate	Spreading pressure (dyne/cm.)
No. 1	47.2	13.4
No. 2	32.8	10.5
No. 3	18.1	8.2
No. 4	10.1	5.1

Table 4.

Piston oil	Palmitic acid μ	Myristic acid μ
Oleic acid	0.10	0.12
Castor oil	0.11	0.18
No. 1	0.11	0.20
No. 2	0.12	0.18
No. 3	0.13	0.22
No. 4	0.13	0.21

From Table 1 and 4 we see that there occurs, generally, a small change in the values of friction coefficient by changing the piston oils of different spreading pressures. However, the value of μ increases definitely with the decrease of spreading pressure. Relatively large difference of μ was detected with 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. In expanded film, molecules arrange rather irregularly even though the film is transferred on the glass plate in compressed state. Myristic acid film may be partly collapsed by the spreading pressure of oleic acid. The film of myristic acid which was deposited in compressed state by oleic acid could not be purely monomolecular.

Subsequently, the effect of the hydrogen ion concentration of the substrate water was investigated. The film transferred from acidic substrate has higher friction coefficient than that transferred from basic substrate. The results are shown in the second column of Table 5. The substrate was distilled water in which barium chloride and potassium bicarbonate were added in the concentration of 10^{-4} mol per litre, and the value of pH was regulated by the addition of ammonia. Stearic acid was used as an film substance. The glass plates on which stearic acid

Table 5.

pH	μ	μ'	% of the fractional conversion to neutral soap
6.50	0.19	0.56	48
6.75	0.16	0.60	54
6.93	0.17	0.54	58
7.39	0.15	0.49	67
8.18	0.12	0.36	80
9.00	0.12	0.24	89
9.26	0.12	0.23	91
9.38	0.12	0.22	92
9.69	0.11	0.16	93

film were deposited by Blodgett's method from the substrate water containing a small quantity of barium ion, were coated by a monomolecular layer consisting of a mixture of stearic acid and barium stearate. These plates were dipped in benzene for about 0.5~1 minute and after withdrawing the plate, the friction coefficients were reinvestigated. It was known that plate coated with the film from basic substrate had relatively low friction coefficient, while the plate coated with the film from acidic substrate had relatively high friction coefficient. According to Langmuir and Schaefer, the film of fatty acid contains metals if the substrate water contains some alkaline earth metals.⁽⁶⁾ The films formed by stearic acid are nearly pure neutral soap when the water is strongly alkaline, while they are of free acids when pH 3. The ratio of free acids and barium or calcium salts varies according to the values of pH. By dipping the plates coated with film in benzene, the free acids may be dissolved whereas the barium salts does not. So that, the friction coefficients of glass surfaces which were covered with the film from acidic substrate, increase considerably by dipping the plate in benzene. However, the plate covered with films from basic substrate show almost the same friction coefficients as before. In the intermediate range of pH the friction coefficients change with pH. The friction coefficients after dipping in benzene (μ') are shown in the third column of Table 5.

The ratio of barium stearate in the film can be calculated by the experimental formula of Langmuir and Schaefer⁽⁶⁾:

$$\log \frac{f}{f'-f} = -2.41+0.367\cdot p\mathrm{H}$$

where f denotes the fractional conversion to neutral soap and f' the limiting value of f for high values of pH and shown in the fourth column of the table. The friction coefficients decrease almost linear with the ratio of the fractional conversion to neutral soap. Fig. 2 shows the result.

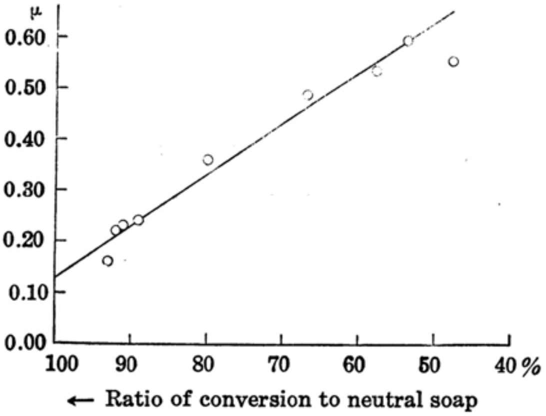

Fig. 2.

In the course of the present experiments, it was experienced that the stearic acid film spread on tap water can be transferred on glass plate more readily than that spread on distilled water only. The force-area relation of the film were studied with stearic acid both on tap water and distilled water using Adam-Jessop's surface balance. The force area curves obtained are reproduced in Fig. 3. It was found that the area occupied by a single molecule is 20.6 sq.

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(6) Langmuir and Schasfer, *J. Am. Chem. Soc.*, **58** (1936), 284.

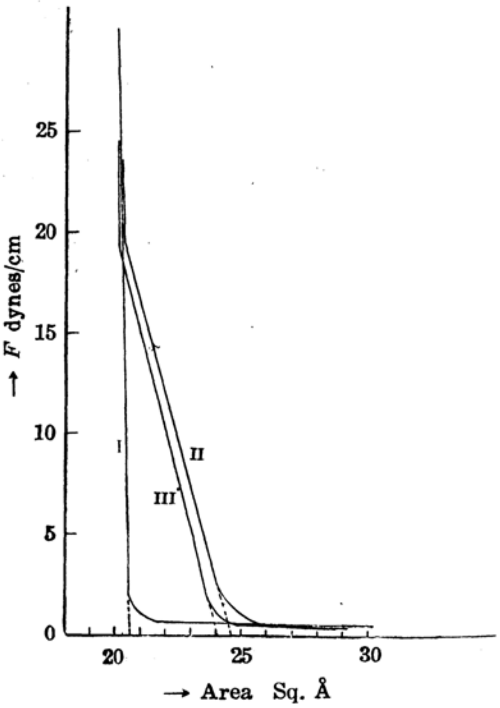

Fig. 3.

Å. on tap water and 24.6 sq. Å. on fresh distilled water. Molecules are more closely packed in the film on tap water than that on distilled water. Molecules in the film on tap water attract each other by lateral forces so that films are stabilised more firmly than the film on distilled water and transferred more readily. On the same reason the films might be deposited on glass plate more readily from basic substrate than from acidic substrate on which molecule occupies larger area.

The effect of the minute amount of metallic ion on the monomolecular films formed by the substance with acidic group was first indicated by Myres and Harkins(7). The small limiting area of stearic acid on tap water may be ascribed to the effect of the presence of calcium ion in tap water. If ammonium oxalate was added to the tap water in the concentration of 0.05 mol per litre, area per single molecule was increased to 24.1 sq. Å. In Fig. 3, I shows the F-A curve of the stearic acid film on tap water, II that on fresh distilled water and III that on tap water added with ammonium oxalate.

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Summary.

(1) The static friction coefficients of glass surfaces covered with the mono- and multi-molecular layers of some long chain acids etc. have been measured.

(2) The friction coefficients of glass covered with monomolecular film of acids are about one tenth of that of clean glass. The friction coefficients of alcohols and esters are somewhat higher but fluctuate considerably.

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(7) R. J. Myers and W. D. Harkins, *Nature*, **139** (1937), 368.

(3) The friction coefficients of multimolecular layers decrease by the increase of their thickness until it becomes five or seven molecular layers, but shows no further reduction.

(4) The effect of compression during the deposition of the film was investigated. The film deposited in high compression state shows low friction coefficient.

(5) The film deposited from basic substrate shows lower friction coefficient than that deposited from acidic substrate.

(6) The force area relations of stearic acid monolayer have been studied on fresh distilled water, on tap water, and on tap water added with ammonium oxalate in relation to the transference of the film on the glass plate.

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